



EPA

Innovative Technology Verification Report

Field Measurement Technology for Mercury in Soil and Sediment

Metorex's X-MET® 2000 X-Ray Fluorescence Technology



Innovative Technology Verification Report

Metorex's X-MET® 2000 X-Ray Fluorescence Technology

Prepared by

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Notice

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Office of Research and Development
Washington, DC 20460

MEASUREMENT AND MONITORING TECHNOLOGY PROGRAM VERIFICATION STATEMENT

TECHNOLOGY TYPE: **Field Measurement Device**

APPLICATION: **Measurement for Mercury**

TECHNOLOGY NAME: **Metorex's X-MET® 2000 (X-MET 2000)**

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VERIFICATION PROGRAM DESCRIPTION

The U.S. Environmental Protection Agency (EPA) created the Superfund Innovative Technology Evaluation (SITE) and Measurement and Monitoring Technology (MMT) Programs to facilitate deployment of innovative technologies through performance verification and information dissemination. The goal of these programs is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. These programs assist and inform those involved in design, distribution, permitting, and purchase of environmental technologies. This document summarizes results of a demonstration of the X-ray fluorescence technology X-MET 2000 developed by Metorex Inc.

PROGRAM OPERATION

Under the SITE and MMT Programs, with the full participation of the technology developers, the EPA evaluates and documents the performance of innovative technologies by developing demonstration plans, conducting field tests, collecting and analyzing demonstration data, and preparing reports. The technologies are evaluated under rigorous quality assurance (QA) protocols to produce well-documented data of known quality. The EPA National Exposure Research Laboratory, which demonstrates field sampling, monitoring, and measurement technologies, selected Science Applications International Corporation as the verification organization to assist in field testing five field measurement devices for mercury in soil and sediment. This demonstration was funded by the SITE Program.

DEMONSTRATION DESCRIPTION

In May 2003, the EPA conducted a field demonstration of the X-MET 2000 and four other field measurement devices for mercury in soil and sediment. This verification statement focuses on the X-MET 2000; a similar statement has been prepared for each of the other four devices. The performance of the X-MET 2000 was compared to that of an off-site laboratory using the reference method, "Test Methods for Evaluating Solid Waste" (SW-846) Method 7471B (modified). To verify a wide range of performance attributes, the demonstration had both primary and secondary objectives. The primary objectives were:

- (1) Determining the instrument sensitivity with respect to the Method Detection Limit (MDL) and Practical Quantitation Limit (PQL);
- (2) Determining the analytical accuracy associated with the field measurement technologies;
- (3) Evaluating the precision of the field measurement technologies;

-
- (4) Measuring the amount of time required for mobilization and setup, initial calibration, daily calibration, sample analysis, and demobilization; and
 - (5) Estimating the costs associated with mercury measurements for the following four categories: capital, labor, supplies, and investigation-derived waste (IDW).

Secondary objectives for the demonstration included:

- (1) Documenting the ease of use, as well as the skills and training required to properly operate the device;
- (2) Documenting potential health and safety concerns associated with operating the device;
- (3) Documenting the portability of the device;
- (4) Evaluating the device durability based on its materials of construction and engineering design; and
- (5) Documenting the availability of the device and associated spare parts.

The X-MET 2000 analyzed 58 field soil samples, 27 field sediment samples, 42 spiked field samples, and 70 performance evaluation (PE) standard reference material (SRM) samples in the demonstration. The field samples were collected in four areas contaminated with mercury, the spiked samples were from these same locations, and the PE samples were obtained from a commercial provider.

Collectively, the field and PE samples provided the different matrix types and the different concentrations of mercury needed to perform a comprehensive evaluation of the X-MET 2000. A complete description of the demonstration and a summary of the results are available in the Innovative Technology Verification Report: "Field Measurement Technology for Mercury in Soil and Sediment—Metorex's X-MET® 2000 X-Ray Fluorescence Technology" (EPA/600/R-03/149).

TECHNOLOGY DESCRIPTION

The Metorex X-MET 2000 analyzer is based on X-ray fluorescence technology. The sample to be measured is irradiated with a radioactive isotope. The isotopes most commonly used in soil analysis are Cd-109 and Am-241. Four different isotope source types are available for use with the X-MET 2000 probes: Fe-55, Cm-244, Cd-109, and Am-241. During the demonstration Cd-109 was used to analyze all 197 soil samples.

An X-ray source can excite characteristic x-rays from an element if the source energy is greater than the absorption edge energy for that element. When an atom absorbs the source X-rays from the isotope source, the incident radiation dislodges electrons from the innermost shells of the atom thereby creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons results in emission of excess energy as X-rays, characteristic of the given atom. The emission of x-rays, in this manner, is termed x-ray fluorescence.

The instrument's detector converts the energies of X-ray quanta to electrical pulses. The pulses are then measured and counted. The intensity (counts in a certain time) from the measured element is proportional to the concentration of the element in the sample. The measurement technique is fast and nondestructive, and multiple elements can be measured simultaneously. The chemical or physical form of the atom does not affect the X-ray energy, because the electrons producing X-rays are not valence (outer) shell electrons. Both identification and quantitation can be accomplished from a single measurement. The high-resolution silicon-PIN detector is stable and accurate, and continuous self-testing and automatic source decay correction ensures the reliability and accuracy of the measurement.

During the demonstration, intrusive measurements were made by placing the probe nose on the sample and pressing the start button on the probe. This opened the source and the sample was exposed to the source. The trigger was then pressed and the sample was measured for a preset time. One analysis takes from 30 seconds to 10 minutes, depending on the desired accuracy. During the demonstration, soil samples from Carson River, Oak Ridge Y-12, and Puget Sound were measured for 240 seconds each, while the Manufacturing Site samples were analyzed for 180 seconds each. Upon completion of the measurement, an assay was displayed. Data collection and analysis were completely automated. Connection to a remote computer, if desired, could allow transfer of the collected data for further evaluation and report generation.

ACTION LIMITS

Action limits and concentrations of interest vary and are project specific. There are, however, action limits which can be considered as potential reference points. The EPA Region IX Preliminary Remedial Goals (PRGs) for mercury are 23 mg/kg in residential soil and 310 mg/kg in industrial soil.

VERIFICATION OF PERFORMANCE

To ensure data usability, data quality indicators for accuracy, precision, representativeness, completeness, comparability, and sensitivity were assessed for the reference method, based on project-specific QA objectives. Key demonstration findings are summarized below for the primary objectives.

Sensitivity: The two primary sensitivity evaluations performed for this demonstration were the MDL and PQL. Both will vary dependent upon whether the matrix is a soil, waste, or aqueous solution. Only soils/sediments were tested during this demonstration, and therefore, MDL calculations and PQL determinations for this evaluation are limited to those matrices. By definition, values measured below the PQL should not be considered accurate or precise and those below the MDL are not distinguishable from background noise.

Method Detection Limit - The evaluation of an MDL requires seven different measurements of a low concentration standard or sample following the procedures established in the 40 Code of Federal Regulations (CFR) Part 136. The evaluation of MDL requires seven different measurements of a low concentration standard or sample. Several standards were evaluated for calculation of the MDL. The range for the calculated MDL is between 16.5 and 26.9 mg/kg. This MDL is very close to the PRG action limit noted above and therefore this should be considered carefully by potential users of this technology for detection of mercury in soils and sediments. Mercury concentrations close to this action limit may not be detected by this technology. The equivalent MDL for the referee laboratory is 0.0026 mg/kg.

Practical Quantitation Limit - The low standard calculations suggest that a PQL for the Metorex field instrument is approximately 64 mg/kg. Given that the definition of a PQL is associated with a defined accuracy and precision, an actual PQL for the Metorex field instrument is difficult to estimate due to the accuracy discrepancy between the X-MET 2000 and the referee laboratory results. The referee laboratory PQL confirmed during the demonstration is 0.005 mg/kg, with a %D <10%.

Accuracy: The results from the X-MET 2000 were compared to the 95% prediction interval for the SRM materials and to the referee laboratory results (Method 7471B). The percentage of Metorex analyses within the 95% prediction interval for SRM materials was only 19% with n = 63. The statistical comparison between the Metorex field data and the referee laboratory results suggests that the two data sets are, in fact, different. Metorex data was found to be both above and below referee laboratory concentrations, and therefore there is no implied or suggested bias. In determining the number of results significantly above or below the value reported by the referee laboratory, 22 of 32 average results are greater than 50% different. Overall, the accuracy evaluations suggest that the Metorex field instrument provides results that are not comparable to the referee laboratory, and not within predicted accuracy specifications as determined by SRM reference materials. Metorex did not bring and utilize calibration standards to the demonstration. The reason for the low accuracy is unknown, and is beyond the scope of this demonstration.

Precision: The precision of the Metorex field analyzer is better than the referee laboratory. The overall average RSD is 20.6% for the referee laboratory, compared to the Metorex average RSD of 9.34%. Both of these RSDs are within the predicted 25% RSD objective for precision; expected from both analytical and sampling variance.

Measurement Time: From the time of sample receipt, Metorex required 18 hours (36 man hours) to prepare a draft data package containing mercury results for 197 samples. Two technicians performed all setup, sample preparation and analysis, and equipment demobilization. However, it was estimated that the second technician worked approximately 25 percent of the time. Individual measurements took 3 or 4 minutes each (after sample preparation), but the total time per analysis averaged 6.9 minutes when all field activities and data package preparation were included, and one-one-fourth technician is included in the calculation.

Measurement Costs: The cost per analysis, based upon 197 samples, when renting the X-MET 2000, is \$33.28 per sample. The cost per analysis for the 197 samples, excluding rental fees, is \$16.02 per sample. Based on the 2-day field demonstration, the total cost for equipment rental and necessary supplies is estimated at \$6,556. The cost breakout by category is: capital costs, 51.9%; supplies, 3.7%; support equipment, 4.2%; labor, 18.3%; and IDW, 22.0%.

Key demonstration findings are summarized below for the secondary objectives.

Ease of Use: Based on observations made during the demonstration, the X-MET 2000 is very easy to operate, requiring one field technician with a high school education and brief training on the analyzer. A training course on instrument operation is included in the purchase price and training is available for \$1000 a day for anyone renting the instrument. The user's manual is easy to follow and the software is menu-driven.

Potential Health and Safety Concerns: No significant health and safety concerns were noted during the demonstration. Potential exposure to radiation from the excitation sources (Cd-109 and Am-241) was the only health and safety concern during the demonstration. The analyzer should never be pointed at anyone while the sources are exposed. No solvents or acids are used for sample preparation.

Portability: The X-MET 2000 is a field-portable, hand-held instrument, consisting of a main unit, external keyboard, battery and a probe. The system is supported with auxiliary devices including a spare battery, battery charger and a water repellent backpack for field transport between sampling locations. The analyzer operates on 110 or 220 volt AC or battery. During the demonstration, the analyzer, operating on 1 NiCd battery, lasted for 4 hours and 10 minutes.

Durability: Based on observations during the demonstration, the main unit and probe were well constructed, field rugged and durable. They are constructed of aluminum and stainless steel. During the two days in which the instrument was observed there was no downtime, maintenance or repairs. The equipment was not apparently effected by the two days of almost continuous rain.

Availability of the Device: The X-MET 2000 is readily available for lease or purchase. The X-MET 2000 rental is available on a limited basis (total of 2 or 3 units). Supplies not provided by Metorex are readily available from supply firms. According to Metorex, no standards are required to analyze samples.

PERFORMANCE SUMMARY

In summary, during the demonstration, the X-MET 2000 exhibited the following desirable characteristics of a field mercury measurement device: (1) good precision, (2) high sample throughput, (3) low measurement costs, and (4) ease of use. During the demonstration the X-MET 2000 was found to have the following limitations: (1) poor accuracy and (2) an MDL that may exceed the residential soil PRG action limit and a PQL that was difficult to define due to poor accuracy. It is recommended that the X-MET 2000 be used only with a strong quality control program in place, utilizing similar matrix standards (i.e., soil) in the field to enable the operator to know when results, with project specific accuracy requirements, are being met. Nonetheless, the X-MET 2000 is a rapid, field rugged measurement device for mercury in soil and sediment.

NOTICE: EPA verifications are based on an evaluation of technology performance under specific, predetermined criteria and appropriate quality assurance procedures. The EPA makes no expressed or implied warranties as to the performance of the technology and does not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's natural resources. Under the mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and scientific support that can be used to solve environmental problems, build the scientific knowledge base needed to manage ecological resources wisely, understand how pollutants affect public health, and prevent or reduce environmental risks.

The National Exposure Research Laboratory is the Agency's center for investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. Goals of the laboratory's research program are to (1) develop and evaluate methods and technologies for characterizing and monitoring air, soil, and water; (2) support regulatory and policy decisions; and (3) provide the scientific support needed to ensure effective implementation of environmental regulations and strategies.

The EPA's Superfund Innovative Technology Evaluation (SITE) Program evaluates technologies designed for characterization and remediation of contaminated Superfund and Resource Conservation and Recovery Act (RCRA) sites. The SITE Program was created to provide reliable cost and performance data in order to speed acceptance and use of innovative remediation, characterization, and monitoring technologies by the regulatory and user community.

Effective monitoring and measurement technologies are needed to assess the degree of contamination at a site, provide data that can be used to determine the risk to public health or the environment, and monitor the success or failure of a remediation process. One component of the EPA SITE Program, the Monitoring and Measurement Technology (MMT) Program, demonstrates and evaluates innovative technologies to meet these needs.

Candidate technologies can originate within the federal government or the private sector. Through the SITE Program, developers are given the opportunity to conduct a rigorous demonstration of their technologies under actual field conditions. By completing the demonstration and distributing the results, the agency establishes a baseline for acceptance and use of these technologies. The MMT Program is managed by the Office of Research and Development's Environmental Sciences Division in Las Vegas, NV.

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Abstract

Metorex's X-MET 2000 X-ray fluorescence analyzer was demonstrated under the U.S. Environmental Protection Agency Superfund Innovative Technology Evaluation Program in May 2003, at the Oak Ridge National Laboratory (ORNL) in Oak Ridge, TN. The purpose of the demonstration was to collect reliable performance and cost data for the X-MET 2000 and four other field measurement devices for mercury in soil and sediment. The key objectives of the demonstration were: 1) determine sensitivity of each instrument with respect to a vendor-generated method detection limit (MDL) and practical quantitation limit (PQL); 2) determine analytical accuracy associated with vendor field measurements using field samples and standard reference materials (SRMs); 3) evaluate the precision of vendor field measurements; 4) measure time required to perform mercury measurements; and 5) estimate costs associated with mercury measurements for capital, labor, supplies, and investigation-derived wastes.

The demonstration involved analysis of SRMs, field samples collected from four sites, and spiked field samples for mercury. The performance results for a given field measurement device were compared to those of an off-site laboratory using reference method, "Test Methods for Evaluating Solid Waste" (SW-846) Method 7471B.

The sensitivity, accuracy, and precision measurements were successfully evaluated. The X-MET 2000 was found to have an MDL of between 16.5 and 26.9 mg/kg and a PQL of approximately 64 mg/kg; however, this PQL was difficult to estimate due to poor instrument accuracy. The instrument was found to be very precise (Metorex had an average relative standard deviation on sample replicates of 9.34% compared to the referee laboratory's 20.6%), but have poor accuracy (22 of 32 samples had a percent difference of greater than 50%). During the demonstration, Metorex required 18 hours (36 man hours) for analysis of 197 samples. The measurement costs were estimated to be \$6,556 for Metorex's X-MET 2000 rental option or \$33.28 per sample; \$16.02 per sample excluding rental costs.

The X-MET 2000 exhibited good ease of use and durability, as well as no major health and safety concerns. The analyzer is lightweight and extremely portable. The demonstration findings collectively indicated that the X-MET 2000 is a rapid and portable field measurement device for mercury in soil.

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Abbreviations, Acronyms, and Symbols

%	Percent
%D	Percent difference
°C	Degrees Celsius
µg/kg	Microgram per kilogram
g/L	Gram per liter
AAS	Atomic absorption spectroscopy
ALSI	Analytical Laboratory Services, Inc.
bgs	Below ground surface
CFR	Code of Federal Regulations
cm	Centimeter
CI	Confidence Interval
COC	Chain of custody
DOE	Department of Energy
EDXRF	Energy Dispersive X-ray Fluorescence
EPA	United States Environmental Protection Agency
eV	Electron volts
FPXRF	Field Portable X-ray Fluorescence
g	Gram
H&S	Health and Safety
Hg	Mercury
HgCl ₂	Mercury (II) chloride
IDL	Instrument detection limit
IDW	Investigation-derived waste
ITVR	Innovative Technology Verification Report
kg	Kilogram
L	Liter
mL/min	Milliliter per Minute
LCS	Laboratory control sample
LEFPC	Lower East Fork Poplar Creek
m	Meter
MDL	Method detection limit
mg	Milligram
mg/kg	Milligram per kilogram
mL	Milliliter
mm	Millimeter
MMT	Monitoring and Measurement Technology
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NERL	National Exposure Research Laboratory
ng	Nanogram

Abbreviations, Acronyms, and Symbols (Continued)

nm	Nanometer
ORD	Office of Research and Development
ORNL	Oak Ridge National Laboratory
ORR	Oak Ridge Reservation
OSWER	Office of Solid Waste and Emergency Response
PPE	Personal protective equipment
ppm	Part per million
PQL	Practical quantitation limit
QA	Quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality control
RPD	Relative percent difference
RSD	Relative standard deviation
SAIC	Science Applications International Corporation
SITE	Superfund Innovative Technology Evaluation
SOP	Standard operating procedure
SRM	Standard reference material
SW-846	Test Methods for Evaluating Solid Waste; Physical/Chemical Methods
TOC	Total organic carbon
TOM	Task Order Manager
UL	Underwriters Laboratory
UEFPC	Upper East Fork of Poplar Creek
Y-12	Y-12 Oak Ridge Security Complex, Oak Ridge, TN

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This document was reviewed for QA by George Brilis of the EPA National Exposure Research Laboratory.

Chapter 1

Introduction

The U.S. Environmental Protection Agency (EPA) under the Office of Research and Development (ORD), National Exposure Research Laboratory (NERL), conducted a demonstration to evaluate the performance of innovative field measurement devices for their ability to measure mercury concentrations in soils and sediments. This Innovative Technology Verification Report (ITVR) presents demonstration performance results and associated costs of Metorex's X-MET 2000 X-ray fluorescence instrument. The vendor-prepared comments regarding the demonstration are presented in Appendix A.

The demonstration was conducted as part of the EPA Superfund Innovative Technology Evaluation (SITE) Monitoring and Measurement Technology (MMT) Program. Mercury contaminated soils and sediments, collected from four sites within the continental U.S., comprised the majority of samples analyzed during the evaluation. Some soil and sediment samples were spiked with mercury (II) chloride (HgCl_2) to provide concentrations not occurring in the field samples. Certified standard reference material (SRM) samples were also used to provide samples with certified mercury concentrations and to increase the matrix variety.

The demonstration was conducted at the Department of Energy (DOE) Oak Ridge National Laboratory (ORNL) in Oak Ridge, TN during the week of May 5, 2003. The purpose of the demonstration was to obtain reliable performance and cost data for field measurement devices in order to 1) provide potential users with a better understanding of the devices' performance and operating costs under well-defined field conditions and 2) provide the instrument vendors with documented results that can assist them in promoting acceptance and use of their devices. The results obtained using the five field mercury measurement devices were compared to the mercury

results obtained for identical sample sets (samples, spiked samples, and SRMs) analyzed at a referee laboratory. The referee laboratory, which was selected prior to the demonstration, used a well-established EPA reference method.

1.1 Description of the SITE Program

Performance verification of innovative environmental technologies is an integral part of the regulatory and research mission of the EPA. The SITE Program was established by EPA's Office of Solid Waste and Emergency Response (OSWER) and ORD under the Superfund Amendments and Reauthorization Act of 1986.

The overall goal of the SITE Program is to conduct performance verification studies and to promote the acceptance of innovative technologies that may be used to achieve long-term protection of human health and the environment. The program is designed to meet three main objectives: 1) identify and remove obstacles to the development and commercial use of innovative technologies; 2) demonstrate promising innovative technologies and gather reliable performance and cost information to support site characterization and cleanup activities; and 3) develop procedures and policies that encourage the use of innovative technologies at Superfund sites, as well as at other waste sites or commercial facilities.

The SITE Program includes the following elements:

- The MMT Program evaluates innovative technologies that sample, detect, monitor, or measure hazardous and toxic substances in soil, water, and sediment samples. These technologies are expected to provide better, faster, or more cost-effective methods for

producing real-time data during site characterization and remediation studies than conventional technologies.

- The Remediation Technology Program conducts demonstrations of innovative treatment technologies to provide reliable performance, cost, and applicability data for site cleanups.
- The Technology Transfer Program provides and disseminates technical information in the form of updates, brochures, and other publications that promote the SITE Program and participating technologies. The Technology Transfer Program also offers technical assistance, training, and workshops in the support of the technologies. A significant number of these activities are performed by EPA's Technology Innovation Office.

The Field Analysis of Mercury in Soils and Sediments demonstration was performed under the MMT Program. The MMT Program provides developers of innovative hazardous waste sampling, detection, monitoring, and measurement devices with an opportunity to demonstrate the performance of their devices under actual field conditions. The main objectives of the MMT Program are as follows:

- Test and verify the performance of innovative field sampling and analytical technologies that enhance sampling, monitoring, and site characterization capabilities.
- Identify performance attributes of innovative technologies that address field sampling, monitoring, and characterization problems in a cost-effective and efficient manner.
- Prepare protocols, guidelines, methods, and other technical publications that enhance acceptance of these technologies for routine use.

The MMT Program is administered by the Environmental Sciences Division of the NERL in Las Vegas, NV. The NERL is the EPA center for investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. The NERL mission components include 1) developing and evaluating methods and technologies for sampling, monitoring, and characterizing water, air, soil, and sediment; 2) supporting regulatory and policy decisions; and 3) providing technical support to ensure the effective implementation of environmental regulations and strategies.

1.2 Scope of the Demonstration

The demonstration project consisted of two separate phases: Phase I involved obtaining information on prospective vendors having viable mercury detection instrumentation. Phase II consisted of field and planning activities leading up to and including the demonstration activities. The following subsections provide detail on both of these project phases.

1.2.1 Phase I

Phase I was initiated by making contact with knowledgeable sources on the subject of "mercury in soil" detection devices. Contacts included individuals within EPA, Science Applications International Corporation (SAIC), and industry where measurement of mercury in soil was known to be conducted. Industry contacts included laboratories and private developers of mercury detection instrumentation. In addition, the EPA Task Order Manager (TOM) provided contacts for "industry players" who had participated in previous MMT demonstrations. SAIC also investigated university and other research-type contacts for knowledgeable sources within the subject area.

These contacts led to additional knowledgeable sources on the subject, which in turn led to various Internet searches. The Internet searches were very successful in finding additional companies involved with mercury detection devices.

All in all, these research activities generated an original list of approximately 30 companies potentially involved in the measurement of mercury in soils. The list included both international and U.S. companies. Each of these companies was contacted by phone or email to acquire further information. The contacts resulted in 10 companies that appeared to have viable technologies.

Due to instrument design (i.e., the instrument's ability to measure mercury in soils and sediments), business strategies, and stage of technology development, only 5 of those 10 vendors participated in the field demonstration portion of phase II.

1.2.2 Phase II

Phase II of the demonstration project involved strategic planning, field-related activities for the demonstration, data analysis, data interpretation, and preparation of the ITVRs. Phase II included pre-demonstration and demonstration activities, as described in the following subsections.

1.2.2.1 Pre-Demonstration Activities

The pre-demonstration activities were completed in the fall 2002. There were six objectives for the pre-demonstration:

- Establish concentration ranges for testing vendors' analytical equipment during the demonstration.
- Collect soil and sediment field samples to be used in the demonstration.
- Evaluate sample homogenization procedures.
- Determine mercury concentrations in homogenized soils and sediments.
- Select a reference method and qualify potential referee laboratories for the demonstration.
- Provide soil and sediment samples to the vendors for self-evaluation of their instruments, as a precursor to the demonstration.

As an integral part of meeting these objectives, a pre-demonstration sampling event was conducted in September 2002 to collect field samples of soils and sediments containing different levels of mercury. The field samples were obtained from the following locations:

- Carson River Mercury site - near Dayton, NV
- Y-12 National Security Complex - Oak Ridge, TN
- A confidential manufacturing facility - eastern U.S.
- Puget Sound - Bellingham Bay, WA

Immediately after collecting field sample material from the sites noted above, the general mercury concentrations in the soils and sediments were confirmed by quick turnaround laboratory analysis of field-collected subsamples using method SW-7471B. The field sample materials were then shipped to a soil preparation laboratory for homogenization. Additional pre-demonstration activities are detailed in Chapter 4.

1.2.2.2 Demonstration Activities

Specific objectives for this SITE demonstration were developed and defined in a Field Demonstration and Quality Assurance Project Plan (QAPP) (EPA Report # EPA/600/R-03/053). The Field Demonstration QAPP is available through the EPA ORD web site

(<http://www.epa.gov/ORD/SITE>) or from the EPA Project Manager. The demonstration objectives were subdivided into two categories: primary and secondary. Primary objectives are goals of the demonstration study that need to be achieved for technology verification. The measurements used to achieve primary objectives are referred to as critical. These measurements typically produce quantitative results that can be verified using inferential and descriptive statistics.

Secondary objectives are additional goals of the demonstration study developed for acquiring other information of interest about the technology that is not directly related to verifying the primary objectives. The measurements required for achieving secondary objectives are considered to be noncritical. Therefore, the analysis of secondary objectives is typically more qualitative in nature and often uses observations and sometimes descriptive statistics.

The field portion of the demonstration involved evaluating the capabilities of five mercury-analyzing instruments to measure mercury concentrations in soil and sediment. During the demonstration, each instrument vendor received three types of samples 1) homogenized field samples referred to as "field samples", 2) certified SRMs, and 3) spiked field samples (spikes).

Spikes were prepared by adding known quantities of HgCl_2 to field samples. Together, the field samples, SRMs, and spikes are referred to as "demonstration samples" for the purpose of this ITVR. All demonstration samples were independently analyzed by a carefully selected referee laboratory. The experimental design for the demonstration is detailed in Chapter 4.

1.3 Mercury Chemistry and Analysis

1.3.1 Mercury Chemistry

Elemental mercury is the only metal that occurs as a liquid at ambient temperatures. Mercury naturally occurs, primarily within the ore, cinnabar, as mercury sulfide (HgS). Mercury easily forms amalgams with many other metals, including gold. As a result, mercury has historically been used to recover gold from ores.

Mercury is ionically stable; however, it is very volatile for a metal. Table 1-1 lists selected physical and chemical properties of elemental mercury.

Table 1-1. Physical and Chemical Properties of Mercury

Properties	Data
Appearance	Silver-white, mobile, liquid.
Hardness	Liquid
Abundance	0.5% in Earth's crust
Density @ 25 °C	13.53 g/mL
Vapor Pressure @ 25 °C	0.002 mm
Volatilizes @	356 °C
Solidifies @	-39 °C

Source: Merck Index, 1983

Historically, mercury releases to the environment included a number of industrial processes such as chloralkali manufacturing, copper and zinc smelting operations, paint application, waste oil combustion, geothermal energy plants, municipal waste incineration, ink manufacturing, chemical manufacturing, paper mills, leather tanning, pharmaceutical production, and textile manufacturing. In addition, industrial and domestic mercury-containing products, such as thermometers, electrical switches, and batteries, are disposed of as solid wastes in landfills (EPA, July 1995). Mercury is also an indigenous compound at many abandoned mining sites and is, of course, found as a natural ore.

At mercury-contaminated sites, mercury exists in mercuric form (Hg^{2+}), mercurous form (Hg_2^{2+}), elemental form (Hg^0), and alkylated form (e.g., methyl or ethyl mercury). Hg_2^{2+} and Hg^{2+} are the more stable forms under oxidizing conditions. Under mildly reducing conditions, both organically bound mercury and inorganic mercury may be degraded to elemental mercury, which can then be converted readily to methyl or ethyl mercury by biotic and abiotic processes. Methyl and ethyl mercury are the most toxic forms of mercury; the alkylated mercury compounds are volatile and soluble in water.

Mercury (II) forms relatively strong complexes with Cl^- and CO_3^{2-} . Mercury (II) also forms complexes with inorganic ligands such as fluoride (F^-), bromide (Br^-), iodide (I^-), sulfate (SO_4^{2-}), sulfide (S^{2-}), and phosphate (PO_4^{3-}) and forms strong complexes with organic ligands, such as sulfhydryl groups, amino acids, and humic and fulvic acids. The insoluble HgS is formed under mildly reducing conditions.

1.3.2 Mercury Analysis

There are several laboratory-based, EPA promulgated methods for the analysis of mercury in solid and liquid hazardous waste matrices. In addition, there are several performance-based methods for the determination of various mercury species. Table 1-2 summarizes the commonly used methods for measuring mercury in both solid and liquid matrices, as identified through a review of the EPA Test Method Index and SW-846. A discussion of the choice of reference method is presented in Chapter 4.

Table 1-2. Methods for Mercury Analysis in Solids or Aqueous Soil Extracts

Method	Analytical Technology	Type(s) of Mercury analyzed	Approximate Concentration Range	Comments
SW-7471B	CVAAS	<ul style="list-style-type: none">• inorganic mercury• organo-mercury	10-2,000 ppb	Manual cold vapor technique widely used for total mercury determinations
SW-7472	ASV	<ul style="list-style-type: none">• inorganic mercury• organo-mercury	0.1-10,000 ppb	Newer, less widely accepted method
SW-7473	TD, amalgamation, and AAS	<ul style="list-style-type: none">• inorganic mercury• organo-mercury	0.2 - 400 ppb	Allows for total decomposition analysis
SW-7474	AFS	<ul style="list-style-type: none">• inorganic mercury• organo-mercury	1 ppb - ppm	Allows for total decomposition analysis; less widely used/reference
EPA 1631	CVAFS	<ul style="list-style-type: none">• inorganic mercury• organo-mercury	0.5 - 100 ppt	Requires "trace" analysis procedures; written for aqueous matrices; Appendix A of method written for sediment/soil samples
EPA 245.7	CVAFS	<ul style="list-style-type: none">• inorganic mercury• organo-mercury	0.5 - 200 ppt	Requires "trace" analysis procedures; written for aqueous matrices; will require dilutions of high-concentration mercury samples
EPA 6200	FPXRF	<ul style="list-style-type: none">• inorganic mercury	>30 mg/kg	Considered a screening protocol

AAS = Atomic Absorption Spectrometry

AAF = Atomic Fluorescence Spectrometry

AFS = Atomic Fluorescence Spectrometry

ASV = Anodic Stripping Voltammetry

CVAAS = Cold Vapor Atomic Absorption Spectrometry

CVAFS = Cold Vapor Atomic Fluorescence Spectrometry

FPXRF = Field Portable X-ray Fluorescence

EPA = U.S. Environmental Protection Agency

mg/kg = milligram per kilogram

ppb = parts per billion

ppm = parts per million

ppt = parts per trillion

SW = solid waste

TD = thermal decomposition

Chapter 2

Technology Description

This chapter contains general information on field portable X-ray fluorescence (FPXRF) analyzers, including the theory of operation, system components, radioisotope sources, and mode of operation. This chapter also provides a detailed description of the Metorex X-MET 2000.

2.1 Description of X-Ray Fluorescence

Energy dispersive X-ray fluorescence (EDXRF) is a method of detecting metals and non-metallic elements in soil and sediment. The method's main strength is as a rapid field screening procedure. Some of the elements that EDXRF can identify are arsenic, barium, cadmium, chromium, copper, lead, mercury, selenium, silver and zinc. Field-portable X-ray fluorescence units that run on battery power and use a radioactive source were developed for use in analysis of lead-based paint. FPXRF analyzers are being used in environmental analyses to identify and characterize sites contaminated with metals, and to guide remedial work.

2.1.1 Theory of EDXRF Analysis

EDXRF analysis detects and measures many elements simultaneously. Generally, EDXRF units can detect and quantify elements from atomic number 19 (potassium) through 94 (plutonium). There are two types of EDXRF units. They can use either an X-ray tube or a radioisotope as a source of X-rays.

In XRF analysis, a process known as the photoelectric effect is used in analyzing samples. Fluorescent X-rays are produced by exposing a sample to an X-ray source that has an excitation energy similar to, but greater than, the binding energy of the inner-shell electrons of the elements in the sample. Some of the source X-rays will be scattered, but a portion will be absorbed by the elements in the sample. Because of their higher energy level, they will

cause ejection of inner shell electrons. The electron vacancies that result will be filled by electrons cascading in from outer shell electrons. However, since electrons in the outer shells have higher energy states than the inner-shell electrons they are replacing, the outer shell electrons must give off energy as they cascade down. The energy is given off in the form of X-rays, and the phenomenon is referred to as X-ray fluorescence (Figure 2-1). Because every element has a different electron shell configuration, each element emits a unique X-ray at a set energy level or wavelength that is characteristic of that element. The elements present in a sample can be identified by observing the energy level of the characteristic X-rays, and they can be quantified using the proportional relationship of the intensity of the X-rays to concentration. The emissions of characteristic X-rays from three electron shells are commonly involved in XRF analysis: the K, L and M shells.

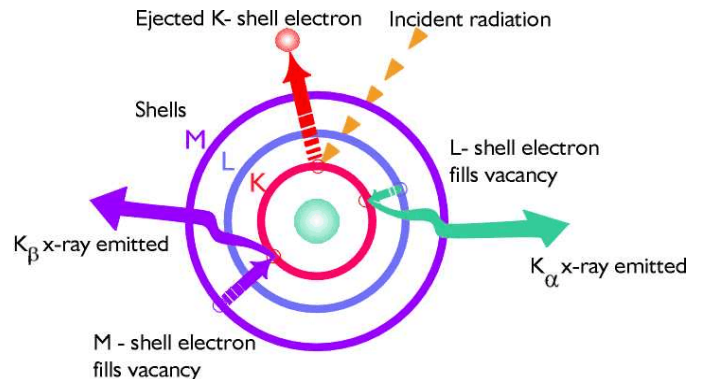


Figure 2-1. X-ray electron orbitals.

2.1.2 System Components

A FPXRF system has two basic components: the radioisotope source and the detector. The source irradiates the sample to produce characteristic X-rays. The detector identifies and measures the intensity of the characteristic X-rays that are emitted in order to identify and quantify the elements present in the sample.

The radioisotope sources commonly used today are Fe-55, Cd-109, and Am-241. FPXRF units have also been developed that use more than one source, allowing them to analyze a greater number and range of elements. Typical arrangements of such multi-source instruments include Cd-109 and Am-241 or Fe-55, Cd-109, and Am-241.

FPXRF units use either gas filled or solid state detectors. Solid state detectors include Si(Li), HgI₂, and silicon-PIN diode. The Si(Li) is capable of the highest resolution, but is quite temperature sensitive. The Si(Li) has a resolution of 170 electron volts (eV) if cooled to at least -90 °C, either with liquid nitrogen or by thermoelectric cooling that uses the Peltier effect. The HgI₂ detector can operate at a moderately subambient temperature, is cooled by use of the Peltier effect, and has a resolution of 270-300 eV. The silicone-PIN diode detector is cooled only slightly by the Peltier effect, and has a resolution of 250 eV.

2.2 Metorex X-MET 2000 Technology Description

The Metorex X-MET 2000 analyzer is based on x-ray fluorescence technology. The sample to be measured is irradiated with a radioactive isotope. The isotopes most commonly used in soil analysis are Cd-109 and Am-241. Four different isotope source types are available for use with the X-MET 2000 probes: Fe-55, Cm-244, Cd-109, and Am-241. During the demonstration, Cd-109 was used to analyze all 197 soil samples. If the energy of radiation from the source is higher than the absorption energy of a certain element, the atoms of that element will be excited, and fluorescent X-ray radiation from that element can be detected with the instrument. The X-ray energies for specific elements are well defined. The instrument's detector converts the energies of X-ray quanta to electrical pulses. The pulses are then detected and counted. The intensity (counts per unit of time) from the measured element is proportional to the concentration of the element in the sample. The measurement technique is fast and nondestructive, and multiple elements can be measured simultaneously. The chemical or physical form of the atom

does not affect the x-ray energy, because the electrons producing x-rays are not valence (outer) shell electrons. Both identification and quantitation can be accomplished from a single measurement. The high-resolution silicon-PIN detector is stable and accurate, and continuous self-testing and automatic source decay correction insures the reliability and accuracy of the measurement results.

Applications and Specifications - The Metorex analyzer can perform analysis on solids, powders, waste water, solutions, slurries, sludge, air particulate matter collected on filters, coating materials and paste samples. The main unit weighs 5.8 kilograms (kg) and has a dimension of 360 millimeters (mm) by 290 mm by 100 mm. The probe has a weight of 1.6 kg and measures 225 mm by 250 mm by 76 mm. Figure 2-2 shows the analyzer used during the demonstration. Required accessories include 2 NiCd batteries, battery charger, and field case for carrying the unit on the shoulder. The NiCd battery operates for approximately 4 hours before needing to be charged. For sample preparation (intrusive analysis), required accessories include polyethylene sample cups, polypropylene film, and a tool for compressing powder or saturated soil samples (pressing tool).



Figure 2-2. Photograph of the X-MET 2000 during the field demonstration.

Operation- After switching the instrument on, the unit should warm up for 15 minutes prior to starting analyses. This will ensure stable and repeatable analyses. In addition, the instrument should be allowed to check its stability regularly by means of the automatic gain control.

When the cap is placed on the probe, the instrument automatically performs a self stabilizing routine. The X-MET 2000 comes factory-calibrated with the help of a universal software package called X-MET 2000 920 calibration software. When measuring with the X-MET 2000, calibration can utilize either fundamental parameters (FPs) or empirical calibration. FP calibration is fast and easy, and does not require user interaction or calibration standards. The standard version analyzes the 25 most common metallic elements from titanium to uranium, including arsenic, selenium, tin, lead, iron, and chromium. The elements analyzed can be customized according to the user's needs. Empirical calibration is used when maximum accuracy is required, for example when measuring trace elements. During the demonstration, empirical calibration was used. For site-specific analysis, the instrument needs to be calibrated either with site-specific or site-typical samples. Between 5-20 samples should be used for calibration. Accurate analytical data must be available for the calibration samples for the elements of interest. The calibration samples must cover the concentration range for each element the user wants to measure.

The measurement is made either by placing the probe on the sample (in situ), or placing the sample in a sample cup (intrusive) and placing the cup on the probe. During the demonstration, intrusive measurements were made by placing the probe nose on the sample and pressing the start button on the probe. This opened the source and the sample was exposed to the source. The trigger was then pressed, and the sample was measured for a preset time. One analysis takes from 30 seconds to 10 minutes, depending on the desired accuracy. During the measurement, there is a time bar on the display indicating the time left for the measurement. The time bar also shows the type of probe used and the source by which the measurement is being made. To change the measurement time, the operator presses the "MEAS Time" button, types in the new time, and presses the "Done" button. During the demonstration, soil samples from Carson River, Oak Ridge Y-12 and Puget Sound had measurement times of 240 seconds each, while the manufacturing site samples were analyzed for 180 seconds

each. The measurement times were based on years of experience operating the analyzer and best engineering practice. On completion of the measurement, an assay was displayed. Data collection, analysis, and management were completely automated. If desired, connection to a remote computer could allow transfer of the collected data for further evaluation and report generation.

In general, when measuring soil, bigger stones and plants should be removed. If sample cups are used, it is advantageous to sieve the sample so that the particle size is homogenous. During the demonstration, the soil samples were sieved and thoroughly homogenized, as discussed in Section 4.3. The water content difference between calibration samples and samples to be analyzed should be less than 25%, in order to minimize error. If the difference is greater than 25%, samples should be dried for more accurate analysis.

Elements with energies close to mercury may interfere with the analysis, if they are present in large quantities. Large quantities of lead, arsenic, and selenium can interfere.

Depending on the data quality needed for the project, longer measurement times can be employed. As measurement times increase, the detector collects a larger number of X-rays from the sample, including more X-rays from other elements that are present at comparable or lower concentrations. The longer the measurement time, the lower the detection limit.

2.3 Developer Contact Information

Additional information about the Metorex X-MET 2000 analyzer can be obtained from the following source:

Metorex, Inc.
John I.H. Patterson
Princeton Crossroads Corp. Center
250 Phillips Blvd., Suite 250
Ewing, NJ 08618
Telephone: (609) 406-9000
Fax: (609) 530-9055
Email: John.patterson@metorexusa.com
Internet: www.metorexusa.com

Chapter 3

Field Sample Collection Locations and Demonstration Site

As previously described in Chapter 1, the demonstration in part tested the ability of all five vendor instruments to measure mercury concentrations in demonstration samples. The demonstration samples consisted of field-collected samples, spiked field samples, and SRMs. The field-collected samples comprised the majority of demonstration samples. This chapter describes the four sites from which the field samples were collected, the demonstration site, and the sample homogenization laboratory. Spiked samples were prepared from these field samples.

Screening of potential mercury-contaminated field sample sites was conducted during Phase I of the project. Four sites were selected for acquiring mercury-contaminated samples that were diverse in appearance, consistency, and mercury concentration. A key criterion was the source of the contamination. These sites included:

- Carson River Mercury site - near Dayton, NV
- The Y-12 National Security Complex (Y-12) - Oak Ridge, TN
- A confidential manufacturing facility - eastern U.S.
- Puget Sound - Bellingham Bay, WA

Site Diversity – Collectively, the four sites provided sampling areas with both soil and sediment, having variable physical consistencies and variable ranges of mercury contamination. Two of the sites (Carson River and Oak Ridge) provided both soil and sediment samples. A third site (a manufacturing facility) provided just soil samples and a fourth site (Puget Sound) provided only sediment samples.

Access and Cooperation – Site representatives were instrumental in providing site access, and in some cases,

guidance on the best areas to collect samples from relatively high and low mercury concentrations. In addition, representatives from the host demonstration site (ORNL) provided a facility for conducting the demonstration.

At three of the sites, the soil and/or sediment sample was collected, homogenized by hand in the field, and subsampled for quick turnaround analysis. These subsamples were sent to analytical laboratories to determine the general range of mercury concentrations at each of the sites. (The Puget Sound site did not require confirmation of mercury contamination due to recently acquired mercury analytical data from another, ongoing research project.) The field-collected soil and sediment samples from all four sites were then shipped to SAIC's GeoMechanics Laboratory for a more thorough sample homogenization (see Section 4.3.1) and subsampled for redistribution to vendors during the pre-demonstration vendor self-evaluations.

All five of the technology vendors performed a self-evaluation on selected samples collected and homogenized during this pre-demonstration phase of the project. For the self-evaluation, the laboratory results and SRM values were supplied to the vendor, allowing the vendor to determine how well it performed the analysis on the field samples. The results were used to gain a preliminary understanding of the field samples collected and to prepare for the demonstration.

Table 3-1 summarizes key characteristics of samples collected at each of the four sites. Also included are the sample matrix, sample descriptions, and sample depth intervals. The analytical results presented in Table 3-1 are based on referee laboratory mercury results for the demonstration samples.

Table 3-1. Summary of Site Characteristics

Site Name	Sampling Area	Sample Matrix	Depth	Description	Hg Concentration Range
Carson River Mercury site	Carson River	Sediment	water/sediment interface	Sandy silt, with some organic debris present (plant stems and leaves)	10 ppb - 50 ppm
	Six Mile Canyon	Soil	3 - 8 cm bgs	Silt with sand to sandy silt	10 ppb - 1,000 ppm
Y-12 National Security Complex	Old Hg Recovery Bldg.	Soil	0 - 1 m bgs	Silty-clay to sandy-gravel	0.1 - 100 ppm
	Poplar Creek	Sediment	0 - 0.5 m bgs	Silt to coarse sandy gravel	0.1 - 100 ppm
Confidential manufacturing site	Former plant building	Soil	3.6 -9 m bgs	Silt to sandy silt	5 - 1,000 ppm
Puget Sound - Bellingham Bay	Sediment layer	Sediment	1.5 - 1.8 m thick	Clayey-sandy silt with various woody debris	10 - 400 ppm
	Underlying Native Material	Sediment	0.3 m thick	Medium-fine silty sands	0.16 - 10 ppm

bgs = below ground surface.

3.1 Carson River

3.1.1 Site Description

The Carson River Mercury site begins near Carson City, NV, and extends downstream to the Lahontan Valley and the Carson Desert. During the Comstock mining era of the late 1800s, mercury was imported to the area for processing gold and silver ore. Ore mined from the Comstock Lode was transported to mill sites, where it was crushed and mixed with mercury to amalgamate the precious metals. The Nevada mills were located in Virginia City, Silver City, Gold Hill, Dayton, Six Mile Canyon, Gold Canyon, and adjacent to the Carson River between New Empire and Dayton. During the mining era, an estimated 7,500 tons of mercury were discharged into the Carson River drainage, primarily in the form of mercury-contaminated tailings (EPA Region 9, 1994).

Mercury contamination is present at Carson River as either elemental mercury and/or inorganic mercury sulfides with less than 1%, if any, methylmercury. Mercury contamination exists in soils present at the former gold and silver mining mill sites; waterways adjacent to the mill sites; and sediment, fish, and wildlife over more than a 50-mile length of the Carson River. Mercury is also present in the sediments and adjacent flood plain of the Carson River, and in the sediments of Lahontan Reservoir, Carson Lake, Stillwater Wildlife Refuge, and Indian Lakes. In addition, tailings with elevated mercury levels are still present at, and around, the historic mill sites, particularly in Six Mile Canyon (EPA, 2002a).

3.1.2 Sample Collection

The Carson River Mercury site provided both soil and sediment samples across the range of contaminant concentrations desired for the demonstration. Sixteen near-surface soil samples were collected between 3-8 cm below ground surface (bgs). Two sediment samples were collected at the water-to-sediment interface. All 18 samples were collected on September 23-24, 2002 with a hand shovel. Samples were collected in Six Mile Canyon and along the Carson River.

The sampling sites were selected based upon historical data from the site. Specific sampling locations in the Six Mile Canyon were selected based upon local terrain and visible soil conditions (e.g., color and particle size). The specific sites were selected to obtain soil samples with as much variety in mercury concentration as possible. These sites included hills, run-off pathways, and dry river bed areas. Sampling locations along the Carson River were selected based upon historical mine locations, local terrain, and river flow.

When collecting the soil samples, approximately 3 cm of surface soil was scraped to the side. The sample was then collected with a shovel, screened through a 6.3-millimeter (mm) (0.25-inch) sieve to remove larger material, and collected in 4-liter (L) sealable bags identified with a permanent marker. The sediment samples were also collected with a shovel, screened through a 6.3-mm sieve to remove larger material, and collected in 4-L sealable bags identified with a permanent marker. Each of the 4-L sealable bags was placed into a second 4-L

sealable bag, and the sample label was placed onto the outside bag. The sediment samples were then placed into 10-L buckets, lidded, and identified with a sample label.

3.2 Y-12 National Security Complex

3.2.1 Site Description

The Y-12 site is located at the DOE ORNL in Oak Ridge, TN. The Y-12 site is an active manufacturing and developmental engineering facility that occupies approximately 800 acres on the northeast corner of the DOE Oak Ridge Reservation (ORR) adjacent to the city of Oak Ridge, TN. Built in 1943 by the U.S. Army Corps of Engineers as part of the World War II Manhattan Project, the original mission of the installation was development of electromagnetic separation of uranium isotopes and weapon components manufacturing, as part of the national effort to produce the atomic bomb. Between 1950 and 1963, large quantities of elemental mercury were used at Y-12 during lithium isotope separation pilot studies and subsequent production processes in support of thermonuclear weapons programs.

Soils at the Y-12 facility are contaminated with mercury in many areas. One of the areas of known high levels of mercury-contaminated soils is in the vicinity of a former mercury use facility (the "Old Mercury Recovery Building" – Building 8110). At this location, mercury-contaminated material and soil were processed in a Nicols-Herschoff roasting furnace to recover mercury. Releases of mercury from this process, and from a building sump used to secure the mercury-contaminated materials and the recovered mercury, have contaminated the surrounding soils (Rothchild, et al., 1984). Mercury contamination also occurred in the sediments of the East Fork of Poplar Creek (DOE, 1998). The Upper East Fork of Poplar Creek (UEFPC) drains the entire Y-12 complex. Releases of mercury via building drains connected to the storm sewer system, building basement dewatering sump discharges, and spills to soils, all contributed to contamination of UEFPC. Recent investigations showed that bank soils containing mercury along the UEFPC were eroding and contributing to mercury loading. Stabilization of the bank soils along this reach of the creek was recently completed.

3.2.2 Sample Collection

Two matrices were sampled at Y-12 in Oak Ridge, TN, creek sediment and soil. A total of 10 sediment samples was collected; one sediment sample was collected from the Lower East Fork of Poplar Creek (LEFPC) and nine sediment samples were collected from the UEFPC. A total

of six soil samples was collected from the Building 8110 area. The sampling procedures that were used are summarized below.

Creek Sediments – Creek sediments were collected on September 24-25, 2002 from the East Fork of Poplar Creek. Sediment samples were collected from various locations in a downstream to upstream sequence (i.e., the downstream LEFPC sample was collected first and the most upstream point of the UEFPC was sampled last).

The sediment samples from Poplar Creek were collected using a commercially available clam-shell sonar dredge attached to a rope. The dredge was slowly lowered to the creek bottom surface, where it was pushed by foot into the sediment. Several drops of the sampler (usually seven or more) were made to collect enough material for screening. On some occasions, a shovel was used to remove overlying "hardpan" gravel to expose finer sediments at depth. One creek sample consisted of creek bank sediments, which was collected using a stainless steel trowel.

The collected sediment was then poured onto a 6.3-mm sieve to remove oversize sample material. Sieved samples were then placed in 12-L sealable plastic buckets. The sediment samples in these buckets were homogenized with a plastic ladle and subsamples were collected in 20-milliliter (mL) vials for quick turnaround analyses.

Soil – Soil samples were collected from pre-selected boring locations September 25, 2002. All samples were collected in the immediate vicinity of the Building 8110 foundation using a commercially available bucket auger. Oversize material was hand picked from the excavated soil because the soil was too wet to be passed through a sieve. The soil was transferred to an aluminum pan, homogenized by hand, and subsampled to a 20-mL vial. The remaining soil was transferred to 4-L plastic containers.

3.3 Confidential Manufacturing Site

3.3.1 Site Description

A confidential manufacturing site, located in the eastern U.S., was selected for participation in this demonstration. The site contains elemental mercury, mercury amalgams, and mercury oxide in shallow sediments (less than 0.3 m deep) and deeper soils (3.65 to 9 m bgs). This site provided soil with concentrations from 5-1,000 mg/kg.

The site is the location of three former processes that resulted in mercury contamination. The first process

involved amalgamation of zinc with mercury. The second process involved the manufacturing of zinc oxide. The third process involved the reclamation of silver and gold from mercury-bearing materials in a retort furnace. Operations led to the dispersal of elemental mercury, mercury compounds such as chlorides and oxides, and zinc-mercury amalgams. Mercury values have been measured ranging from 0.05 to over 5,000 mg/kg, with average values of approximately 100 mg/kg.

3.3.2 Sample Collection

Eleven subsurface soil samples were collected on September 24, 2002. All samples were collected with a Geoprobe® unit using plastic sleeves. All samples were collected at the location of a former facility plant. Drilling locations were determined based on historical data provided by the site operator. The intention was to gather soil samples across a range of concentrations. Because the surface soils were from relatively clean fill, the sampling device was pushed to a depth of 3.65 m using a blank rod. Samples were then collected at pre-selected depths ranging from 3.65 to 9 m bgs. Individual cores were 1-m long. The plastic sleeve for each 1-m core was marked with a permanent marker; the depth interval and the bottom of each core was marked. The filled plastic tubes were transferred to a staging table where appropriate depth intervals were selected for mixing. Selected tubes were cut into 0.6-m intervals, which were emptied into a plastic container for premixing soils. When feasible, soils were initially screened to remove materials larger than 6.3-mm in diameter. In many cases, soils were too wet and clayey to allow screening; in these cases, the soil was broken into pieces by hand and, by using a wooden spatula, oversize materials were manually removed. These soils (screened or hand sorted) were then mixed until the soil appeared visually uniform in color and texture. The mixed soil was then placed into a 4-L sample container for each chosen sample interval. A subsample of the mixed soil was transferred into a 20-mL vial, and it was sent for quick turnaround mercury analysis. This process was repeated for each subsequent sample interval.

3.4 Puget Sound

3.4.1 Site Description

The Puget Sound site consists of contaminated offshore sediments. The particular area of the site used for collecting demonstration samples is identified as the Georgia Pacific, Inc. Log Pond. The Log Pond is located within the Whatcom Waterway in Bellingham Bay, WA, a

well-established heavy industrial land use area with a maritime shoreline designation. Log Pond sediments measure approximately 1.5 to 1.8-m thick, and contain various contaminants including mercury, phenols, polyaromatic hydrocarbons, polychlorinated biphenyls, and wood debris. Mercury was used as a preservative in the logging industry. The area was capped in late 2000 and early 2001 with an average of 7 feet of clean capping material, as part of a Model Toxics Control Act interim cleanup action. The total thickness ranges from approximately 0.15 m along the site perimeter to 3 m within the interior of the project area. The restoration project produced 2.7 acres of shallow sub-tidal and 2.9 acres of low intertidal habitat, all of which had previously exceeded the Sediment Management Standards cleanup criteria (Anchor Environmental, 2001).

Mercury concentrations have been measured ranging from 0.16 to 400 mg/kg (dry wt). The majority (98%) of the mercury detected in near-shore ground waters and sediments of the Log Pond is believed to be comprised of complexed divalent (Hg^{2+}) forms such as mercuric sulfide (Bothner, et al., 1980 and Anchor Environmental, 2000).

3.4.2 Sample Collection

Science Applications International Corporation (SAIC) is currently performing a SITE remedial technology evaluation in the Puget Sound (SAIC, 2002). As part of ongoing work at that site, SAIC collected additional sediment for use during this MMT project. Sediment samples collected on August 20-21, 2002 from the Log Pond in Puget Sound were obtained beneath approximately 3-6 m of water, using a vibra-coring system capable of capturing cores to 0.3 m below the proposed dredging prism. The vibra-corer consisted of a core barrel attached to a power head. Aluminum core tubes, equipped with a stainless steel "eggshell" core catcher to retain material, were inserted into the core barrel. The vibra-core was lowered into position on the bottom and advanced to the appropriate sampling depth. Once sampling was completed, the vibra-core was retrieved and the core liner removed from the core barrel. The core sample was examined at each end to verify that sufficient sediment was retained for the particular sample. The condition and quantity of material within the core was then inspected to determine acceptability.

The following criteria were used to verify whether an acceptable core sample was collected:

- Target penetration depth (i.e., into native material) was achieved.

- Sediment recovery of at least 65% of the penetration depth was achieved.
- Sample appeared undisturbed and intact without any evidence of obstruction/blocking within the core tube or catcher.

The percent sediment recovery was determined by dividing the length of material recovered by the depth of core penetration below the mud line. If the sample was deemed acceptable, overlying water was siphoned from the top of the core tube and each end of the tube capped and sealed with duct tape. Following core collection, representative samples were collected from each core section representing a different vertical horizon. Sediment was collected from the center of the core that had not been smeared by, or in contact with, the core tube. The volumes removed were placed in a decontaminated stainless steel bowl or pan and mixed until homogenous in texture and color (approximately 2 minutes).

After all sediment for a vertical horizon composite was collected and homogenized, representative aliquots were placed in the appropriate pre-cleaned sample containers. Samples of both the sediment and the underlying native material were collected in a similar manner. Distinct layers of sediment and native material were easily recognizable within each core.

3.5 Demonstration Site

The demonstration was conducted in a natural environment, outdoors, in Oak Ridge, TN. The area was a grass covered hill with some parking areas, all of which were surrounded by trees. Building 5507, in the center of the demonstration area, provided facilities for lunch, break, and sample storage for the project and personnel.

Most of the demonstration was performed during rainfall events ranging from steady to torrential. Severe puddling of rain occurred to the extent that boards needed to be placed under chairs to prevent them from sinking into the ground. Even when it was not raining, the relative humidity was high, ranging from 70.6 to 98.3 percent. Between two and four of the tent sides were used to keep rainfall from damaging the instruments. The temperature in the afternoons ranged from 65-70 degrees Fahrenheit, and the wind speed was less than 10 mph. The latitude is 36°N, the longitude 35°W, and the elevation 275 m. (Figure 3-1 is a photograph of the site during the demonstration and Figure 3-2 is a photograph of the location.)



Figure 3-1. Tent and field conditions during the demonstration at Oak Ridge, TN.



Figure 3-2. Demonstration site and Building 5507.

3.6 SAIC GeoMechanics Laboratory

Sample homogenization was completed at the SAIC GeoMechanics Laboratory in Las Vegas, NV. This facility is an industrial-type building with separate facilities for personnel offices and material handling. The primary function of the laboratory is for rock mechanics studies. The laboratory has rock mechanics equipment, including

sieves, rock crushers, and sample splitters. The personnel associated with this laboratory are experienced in the areas of sample preparation and sample homogenization. In addition to the sample homogenization equipment, the laboratory contains several benches, tables, and open space. Mercury air monitoring equipment was used during the sample preparation activities for personnel safety.

Chapter 4 Demonstration Approach

This chapter describes the demonstration approach that was used for evaluating the field mercury measurement technologies at ORNL in May 2003. It presents the objectives, design, sample preparation and management procedures, and the reference method confirmatory process used for the demonstration.

4.1 Demonstration Objectives

The primary goal of the SITE MMT Program is to develop reliable performance and cost data on innovative, field-ready measurement technologies. A SITE demonstration must provide detailed and reliable

performance and cost data in order that potential technology users have adequate information needed to make sound judgements regarding an innovative technology's applicability to a specific site and to be able to compare the technology to conventional laboratory technologies.

Table 4-1 summarizes the project objectives for this demonstration. In accordance with *QAPP Requirements for Applied Research Projects (EPA, 1998)*, the technical project objectives for the demonstration were categorized as primary and secondary.

Table 4-1. Demonstration Objectives

Objective	Description	Method of Evaluation
Primary Objectives		
Primary Objective # 1	Determine sensitivity of each instrument with respect to vendor-generated MDL and PQL.	Independent laboratory confirmation of SRMs, field samples, and spiked field samples.
Primary Objective # 2	Determine potential analytical accuracy associated with vendor field measurements.	
Primary Objective # 3	Evaluate the precision of vendor field measurements.	
Primary Objective # 4	Measure time required to perform five functions related to mercury measurements: 1) mobilization and setup, 2) initial calibration, 3) daily calibration, 4) sample analysis, and 5) demobilization.	Documentation during demonstration; vendor-provided information.
Primary Objective # 5	Estimate costs associated with mercury measurements for the following four categories: 1) capital, 2) labor, 3) supplies, and 4) investigation-derived wastes.	
Secondary Objectives		
Secondary Objective # 1	Document ease of use, skills, and training required to operate the device properly.	Documentation of observations during demonstration; vendor-provided information.
Secondary Objective # 2	Document potential H&S concerns associated with operating the device.	
Secondary Objective # 3	Document portability of the device.	
Secondary Objective # 4	Evaluate durability of device based on materials of construction and engineering design.	Post-demonstration investigation.
Secondary Objective # 5	Document the availability of the device and its spare parts.	

Critical data support primary objectives and noncritical data is used to support secondary objectives. With the exception of the cost information, primary objectives required the use of quantitative results to draw conclusions regarding technology performance. Secondary objectives pertained to information that was useful and did not necessarily require the use of quantitative results to draw conclusions regarding technology performance.

4.2 Demonstration Design

4.2.1 Approach for Addressing Primary Objectives

The purpose of this demonstration was to evaluate the vendor's instrumentation against a standard laboratory procedure. In addition, an overall average relative standard deviation (RSD) was calculated for all measurements made by the vendor and the referee laboratory. RSD comparisons used descriptive statistics, not inferential statistics, between the vendor and laboratory results. Other statistical comparisons (both inferential and descriptive) for sensitivity, precision, and accuracy were used, depending upon actual demonstration results.

The approach for addressing each of the primary objectives is discussed in the following subsections. A detailed explanation of the precise statistical determination used for evaluating primary objectives No. 1 through No. 3 is presented in Chapter 6.

4.2.1.1 Primary Objective #1: Sensitivity

Sensitivity is the ability of a method or instrument to discriminate between small differences in analyte concentration (EPA, 2002b). It can be discussed in terms of an instrument detection limit (IDL), a method detection limit (MDL), and a practical quantitation limit (PQL). MDL is not a measure of sensitivity in the same respect as an IDL or PQL. It is a measure of precision at a predetermined, usually low, concentration. The IDL pertains to the ability of the instrument to determine with confidence the difference between a sample that contains the analyte of interest at a low concentration and a sample that does not contain that analyte. The IDL is generally considered to be the minimum true concentration of an analyte producing a non-zero signal that can be distinguished from the signals generated when no concentration of the analyte is present and with an adequate degree of certainty.

The IDL is not rigidly defined in terms of matrix, method, laboratory, or analyst variability, and it is not usually associated with a statistical level of confidence. IDLs are thus usually lower than MDLs and rarely serve a purpose in terms of project objectives (EPA, 2002b). The PQL defines a specific concentration with an associated level of accuracy. The MDL defines a lower limit at which a method measurement can be distinguished from background noise. The PQL is a more meaningful estimate of sensitivity. The MDL and PQL were chosen as the two distinct parameters for evaluating sensitivity. The approach for addressing each of these indicator parameters is discussed separately in the following paragraphs.

MDL

MDL is the estimated measure of sensitivity as defined in 40 Code of Federal Regulations (CFR) Part 136. The purpose of the MDL measurement is to estimate the concentration at which an individual field instrument is able to detect a minimum concentration that is statistically different from instrument background or noise. Guidance for the definition of the MDL is provided in EPA G-5i (EPA, 2002b).

The determination of an MDL usually requires seven different measurements of a low concentration standard or sample. Following procedures established in 40 CFR Part 136 for water matrices, the demonstration MDL definition is as follows:

$$MDL = t_{(n-1, 0.99)} s$$

where: $t_{(n-1, 0.99)}$	=	99 th percentile of the t-distribution with n-1 degrees of freedom
n	=	number of measurements
s	=	standard deviation of replicate measurements

PQL

The PQL is another important measure of sensitivity. The PQL is defined in EPA G-5i as the lowest level an instrument is capable of producing a result that has significance in terms of precision and bias. (Bias is the difference between the measured value and the true value.) It is generally considered the lowest standard on the instrument calibration curve. It is often 5-10 times higher than the MDL, depending upon the analyte, the instrument being used, and the method for analysis; however it should not be rigidly defined in this manner.

During the demonstration, the PQL was to be defined by the vendor's reported lower limit of calibration or based upon lower concentration samples or SRMs. The evaluation of vendor-reported results for the PQL included a determination of the percent difference (%D) between their calculated value and true value. The true value is considered the value reported by the referee laboratory for field samples or spiked field samples, or, in the case of SRMs, the certified value provided by the supplier. The equation used for the %D calculation is:

$$\%D = \frac{|C_{\text{true}} - C_{\text{calculated}}|}{C_{\text{true}}} \times 100$$

where: C_{true} = true concentration as determined by the referee laboratory or SRM reference value
 $C_{\text{calculated}}$ = calculated test sample concentration

The PQL and %D were reported for the vendor. The %D for the referee laboratory, at the same concentration, was also reported for purposes of comparison. No statistical comparison was made between these two values; only a descriptive comparison was made for purposes of this evaluation. (The %D requirement for the referee laboratory was defined as 10% or less. The reference method PQL was approximately 10 µg/kg).

4.2.1.2 Primary Objective #2: Accuracy

Accuracy was calculated by comparing the measured value to a known or true value. For purposes of this demonstration, three separate types of samples were used to evaluate accuracy. These included: 1) SRMs, 2) field samples collected from four separate mercury-contaminated sites, and 3) spiked field samples. Four sites were used for evaluation of the Metorex field instrument. Samples representing field samples and spiked field samples were prepared at the SAIC GeoMechanics Laboratory. In order to prevent cross contamination, SRMs were prepared in a separate location. Each of these standards is discussed separately in the following paragraphs.

SRMs

The primary standards used to determine accuracy for this demonstration were SRMs. SRMs provided very tight statistical comparisons, although they did not provide all

matrices of interest nor all ranges of concentrations. The SRMs were obtained from reputable suppliers, and had reported concentrations at associated 95% confidence intervals (CIs) and 95% prediction intervals. Prediction intervals were used for comparison because they represent a statistically infinite number of analyses, and therefore, would include all possible correct results 95% of the time. All SRMs were analyzed by the referee laboratory and selected SRMs were analyzed by the vendor, based upon instrument capabilities and concentrations of SRMs that could be obtained. Selected SRMs covered an appropriate range for each vendor. Replicate SRMs were also analyzed by the vendor and the referee laboratory.

The purpose for SRM analysis by the referee laboratory was to provide a check on laboratory accuracy. During the pre-demonstration, the referee laboratory was chosen, in part, based upon the analysis of SRMs. This was done to ensure a competent laboratory would be used for the demonstration. Because of the need to provide confidence in laboratory analysis during the demonstration, the referee laboratory analyzed SRMs as an ongoing check for laboratory bias.

Evaluation of vendor and laboratory analysis of SRMs was performed as follows. Accuracy was reported for individual sample concentrations of replicate measurements made at the same concentration.

Two-tailed 95% CIs were computed according to the following equation:

$$\bar{x} \pm t_{(n-1, 0.975)} \cdot s / \sqrt{n}$$

where: $t_{(n-1, 0.975)}$ = 97.5th percentile of the t-distribution with n-1 degrees of freedom
 n = number of measurements
 s = standard deviation of replicate measurements

The number of vendor-reported SRM results and referee laboratory-reported SRM results that were within the associated 95% prediction interval were evaluated. Prediction intervals were computed in a manner similar to the CI, except that the Students "t" value use "n" equal to infinity and, because the prediction intervals represented "n" approaching infinity, the square root of "n" was dropped from the equation.

A final measure of accuracy determined from SRMs is a frequency distribution that shows the percentage of vendor-

reported measurements that are within a specified window of the reference value or referee laboratory reported value. For example, a distribution within a 30% window of a reported concentration, within a 50% window, and outside a 50% window of a reported concentration. This distribution aspect could be reported as average concentrations of replicate results from the vendor for a particular concentration and matrix compared to the same sample from the laboratory. These are descriptive statistics and are used to better describe comparisons, but they are not intended as inferential tests.

Field Samples

The second accuracy standard used for this demonstration was actual field samples collected from four separate mercury-contaminated sites. This accuracy determination consisted of a comparison of vendor-reported results for field samples to the referee laboratory results for the same field samples. The field samples were used to ensure that "real-world" samples were tested for each vendor. The field samples consisted of variable mercury concentrations within varying soil and sediment matrices. The referee laboratory results are considered the standard for comparison to each vendor.

Vendor sample results for a given field sample were compared to replicates analyzed by the laboratory for the same field sample. (A hypothesis test was used with $\alpha = 0.01$. The null hypothesis was that sample results were similar. Therefore, if the null hypothesis is rejected, then the sample sets are considered different.) Comparisons for a specific matrix or concentration were made in order to provide additional information on that specific matrix or concentration. Comparison of the vendor values to laboratory values were similar to the comparisons noted previously for SRMs except that a more definitive or inferential statistical evaluation was used. $\alpha = 0.01$ was used to help mitigate inter-laboratory variability. Additionally, an aggregate analysis, was used to mitigate statistical anomalies (see Section 6.1.2).

Spiked Field Samples

The third accuracy standard for this demonstration was spiked field samples. These spiked field samples were analyzed by the vendors and by the referee laboratory in replicate in order to provide additional measurement comparisons to a known value. Spikes were prepared to cover additional concentrations not available from SRMs or the samples collected in the field. They were grouped with the field sample comparison noted above.

4.2.1.3 Primary Objective #3: Precision

Precision can be defined as the degree of mutual agreement of independent measurements generated through repeated application of a process under specified conditions. Precision is usually thought of as repeatability of a specific measurement, and it is often reported as RSD. The RSD is computed from a specified number of replicates. The more replications of a measurement, the more confidence is associated with a reported RSD. Replication of a measurement may be as few as 3 separate measurements, to 30 or more measurements of the same sample, dependent upon the degree of confidence desired in the specified result. The precision of an analytical instrument may vary depending upon the matrix being measured, the concentration of the analyte, and whether the measurement is made for an SRM or a field sample.

The experimental design for this demonstration included a mechanism to evaluate the precision of the vendors' technologies. Field samples from the four mercury-contaminated field sites were evaluated by each vendor's analytical instrument. During the demonstration, concentrations were predetermined only as low, medium, or high. Ranges of test samples (field samples, SRMs, and spikes) were selected to cover the appropriate analytical ranges of each vendor's instrumentation. It was known prior to the demonstration that not all vendors were capable of measuring similar concentrations (i.e., some instruments were better at measuring low concentrations and others were geared toward higher concentration samples or had other attributes such as cost or ease of use that defined the specific attributes of their technology). Because of this fact, not all vendors analyzed the same samples.

During the demonstration, the vendor's instrument was tested with samples from the four different sites, having different matrices when possible (i.e., depending upon available concentrations) and having different concentrations (high, medium, and low) using a variety of samples. Sample concentrations for an individual instrument were chosen based upon vendor attributes in terms of expected low, medium, and high concentrations that the particular instrument was capable of measuring.

The referee laboratory measured replicates of all samples. The results were used for precision comparisons to the individual vendor. The RSD for the vendor and the laboratory were calculated individually, using the following equation:

$$\%RSD = \frac{s}{\bar{x}} \times 100$$

where: s = standard deviation of replicate results
 \bar{x} = mean value of replicate results

Using descriptive statistics, differences between vendor RSD and referee laboratory RSD were determined. This included RSD comparisons based upon concentration, SRMs, field samples, and different sites. In addition, an overall average RSD was calculated for all measurements made by the vendor and the laboratory. RSD comparisons were based upon descriptive statistical evaluations between the vendor and the laboratory, and results were compared accordingly.

4.2.1.4 Primary Objective #4: Time per Analysis

The amount of time required for performing the analysis was measured and reported for five categories:

- Mobilization and setup
- Initial calibration
- Daily calibration
- Sample analyses
- Demobilization

Mobilization and setup included the time needed to unpack and prepare the instrument for operation. Initial calibration included the time to perform the vendor recommended on-site calibrations. Daily calibration included the time to perform the vendor-recommended calibrations on subsequent field days. (Note that this could have been the same as the initial calibration, a reduced calibration, or none.) Sample analyses included the time to prepare, measure, and calculate results for the demonstration and the necessary quality control (QC) samples performed by the vendor.

The time per analysis was determined by dividing the total amount of time required to perform the analyses by the number of samples analyzed (197). In the numerator, sample analysis time included preparation, measurement, and calculation of results for demonstration samples and necessary QC samples performed by the vendor. In the denominator, the total number of analyses included only demonstration samples analyzed by the vendor, not QC analyses nor reanalyses of samples.

Downtime that was required or that occurred between sample analyses as a part of operation and handling was considered a part of the sample analysis time. Downtime

occurring due to instrument breakage or unexpected maintenance was not counted in the assessment, but it is noted in this final report as an additional time. Any downtime caused by instrument saturation or memory effect was addressed, based upon its frequency and impact on the analysis.

Unique time measurements are also addressed in this report (e.g., if soil samples were analyzed directly, and sediment samples required additional time to dry before the analyses started, then a statement was made noting that soil samples were analyzed in X amount of hours, and that sediment samples required drying time before analysis).

Recorded times were rounded to the nearest 15-minute interval. The number of vendor personnel used was noted and factored into the time calculations. No comparison on time per analysis is made between the vendor and the referee laboratory.

4.2.1.5 Primary Objective #5: Cost

The following four cost categories were considered to estimate costs associated with mercury measurements:

- Capital costs
- Labor costs
- Supply costs
- Investigation-derived waste (IDW) disposal costs

Although both vendor and laboratory costs are presented, the calculated costs were not compared with the referee laboratory. A summary of how each cost category was estimated for the measurement device is provided below.

- The capital cost was estimated based on published price lists for purchasing, renting, or leasing each field measurement device. If the device was purchased, the capital cost estimate did not include salvage value for the device after work was completed.
- The labor cost was based on the number of people required to analyze samples during the demonstration. The labor rate was based on a standard hourly rate for a technician or other appropriate operator. During the demonstration, the skill level required was confirmed based on vendor input regarding the operation of the device to produce mercury concentration results and observations made in the field. The labor costs were based on: 1) the actual number of hours required to complete all analyses, quality assurance (QA), and reporting; and 2) the assumption that a technician who worked for a portion of a day was paid for an entire 8-hour day.

- The supply costs were based on any supplies required to analyze the field and SRM samples during the demonstration. Supplies consisted of items not included in the capital category, such as extraction solvent, glassware, pipettes, spatulas, agitators, and similar materials. The type and quantity of all supplies brought to the field and used during the demonstration were noted and documented.

Any maintenance and repair costs during the demonstration were documented or provided by the vendor. Equipment costs were estimated based on this information and standard cost analysis guidelines used in the SITE Program.

- The IDW disposal costs included decontamination fluids and equipment, mercury-contaminated soil and sediment samples, and used sample residues. Contaminated personal protective equipment (PPE) normally used in the laboratory was placed into a separate container. The disposal costs for the IDW were included in the overall analytical costs for each vendor.

After all of the cost categories were estimated, the cost per analysis was calculated. This cost value was based on the number of analyses performed. As the number of samples analyzed increased, the initial capital costs and certain other costs were distributed across a greater number of samples. Therefore, the per unit cost decreased. For this reason, two costs were reported: 1) the initial capital costs and 2) the operating costs per analysis. No comparison to the referee laboratory's method cost was made; however,

a generic cost comparison is made. Additionally, when determining laboratory costs, the associated cost for laboratory audits and data validation should be considered.

4.2.2 Approach for Addressing Secondary Objectives

Secondary objectives were evaluated based on observations made during the demonstration. Because of the number of vendors involved, technology observers were required to make simultaneous observations of two vendors each during the demonstration. Four procedures were implemented to ensure that these subjective observations made by the observers were as consistent as possible.

First, forms were developed for each of the five secondary objectives. These forms assisted in standardizing the observations. Second, the observers met each day before the evaluations began, at significant break periods, and after each day of work to discuss and compare observations regarding each device. Third, an additional observer was assigned to independently evaluate only the secondary objectives in order to ensure that a consistent approach was applied in evaluating these objectives. Finally, the SAIC TOM circulated among the evaluation staff during the demonstration to ensure that a consistent approach was being followed by all personnel. Table 4-2 summarizes the aspects observed during the demonstration for each secondary objective. The individual approaches to each of these objectives are detailed further in the following subsections.

Table 4-2. Summary of Secondary Objective Observations Recorded During the Demonstration

General Information	SECONDARY OBJECTIVE			
	Secondary Objective # 1 Ease of Use	Secondary Objective # 2 H&S Concerns	Secondary Objective # 3 Instrument Portability	Secondary Objective # 4 Instrument Durability
- Vendor Name	- No. of Operators	- Instrument Certifications	- Instrument Weight	- Materials of Construction
- Observer Name	- Operator Names/Titles	- Electrical Hazards	- Instrument Dimensions	- Quality of Construction
- Instrument Type	- Operator Training	- Chemicals Used	- Power Sources	- Max. Operating Temp.
- Instrument Name	- Training References	- Radiological Sources	- Packaging	- Max. Operating Humidity
- Model No.	- Instrument Setup Time	- Hg Exposure Pathways	- Shipping & Handling	- Downtime
- Serial No.	- Instrument Calibration Time	- Hg Vapor Monitoring		- Maintenance Activities
	- Sample Preparation Time	- PPE Requirements		- Repairs Conducted
	- Sample Measurement Time	- Mechanical Hazards		
		- Waste Handling Issues		
H&S =	Health and Safety			
PPE =	Personal Protective Equipment			

4.2.2.1 Secondary Objective #1: Ease of Use

The skills and training required for proper device operation were noted; these included any degrees or specialized training required by the operators. This information was gathered by interviews (i.e., questioning) of the operators. The number of operators required was also noted. This objective was also evaluated by subjective observations regarding the ease of equipment use and major peripherals required to measure mercury concentrations in soils and sediments. The operating manual was evaluated to determine if it is easily useable and understandable.

4.2.2.2 Secondary Objective #2: Health and Safety Concerns

Health and safety (H&S) concerns associated with device operation were noted during the demonstration. Criteria included hazardous materials used, the frequency and likelihood of potential exposures, and any direct exposures observed during the demonstration. In addition, any potential for exposure to mercury during sample digestion and analysis was evaluated, based upon equipment design. Other H&S concerns, such as basic electrical and mechanical hazards, were also noted. Equipment certifications, such as Underwriters Laboratory (UL), were documented.

4.2.2.3 Secondary Objective #3: Portability of the Device

The portability of the device was evaluated by observing transport, measuring setup and tear down time, determining the size and weight of the unit and peripherals, and assessing the ease with which the instrument was repackaged for movement to another location. The use of battery power or the need for an AC outlet was also noted.

4.2.2.4 Secondary Objective #4: Instrument Durability

The durability of each device and major peripherals was assessed by noting the quality of materials and construction. All device failures, routine maintenance, repairs, and downtime were documented during the demonstration. No specific tests were performed to evaluate durability; rather, subjective observations were made using a field form as guidance.

4.2.2.5 Secondary Objective #5: Availability of Vendor Instruments and Supplies

The availability of each device was evaluated by determining whether additional units and spare parts are readily available from the vendor or retail stores. The vendor's office (or a web page) and/or a retail store was

contacted to identify and determine the availability of supplies of the tested measurement device and spare parts. This portion of the evaluation was performed after the field demonstration, in conjunction with the cost estimate.

4.3 Sample Preparation and Management

4.3.1 Sample Preparation

4.3.1.1 Field Samples

Field samples were collected during the pre-demonstration portion of the project, with the ultimate goal of producing a set of consistent test soils and sediments to be distributed among all participating vendors and the referee laboratory for analysis during the demonstration. Samples were collected from the following four sites:

- Carson River Mercury site (near Dayton, NV)
- Y-12 National Security Complex (Oak Ridge, TN)
- Manufacturing facility (eastern U.S.)
- Puget Sound (Bellingham, WA)

The field samples collected during the pre-demonstration sampling events comprised a variety of matrices, ranging from material having a high clay content to material composed mostly of gravelly, coarse sand. The field samples also differed with respect to moisture content; several were collected as wet sediments. Table 4-3 shows the number of distinct field samples that were collected from each of the four field sites.

Prior to the start of the demonstration, the field samples selected for analysis during the demonstration were processed at the SAIC GeoMechanics Laboratory in Las Vegas, NV. The specific sample homogenization procedure used by this laboratory largely depended on the moisture content and physical consistency of the sample. Two specific sample homogenization procedures were developed and tested by SAIC at the GeoMechanics Laboratory during the pre-demonstration portion of the project. The methods included a non-slurry sample procedure and a slurry sample procedure.

A standard operating procedure (SOP) was developed detailing both methods. The procedure was found to be satisfactory, based upon the results of replicate samples during the pre-demonstration. This SOP is included as Appendix A of the *Field Demonstration Quality Assurance Project Plan* (SAIC, April 2003, EPA/600/R-03/053). Figure 4-1 summarizes the homogenization steps of the SOP, beginning with sample mixing. This procedure was used

for preparing both pre-demonstration and demonstration samples. Prior to the mixing process (i.e., Step 1 in Figure 4-1), all field samples being processed were visually inspected to ensure that oversized materials were removed and that there were no clumps that would hinder homogenization. Non-slurry samples were air-dried in accordance with the SOP so that they could be passed multiple times through a riffle splitter. Due to the high

moisture content of many of the samples, they were not easily air-dried and could not be passed through a riffle splitter while wet. Samples with very high moisture contents, termed “slurries,” were not air-dried, and bypassed the riffle splitting step. The homogenization steps for each type of matrix are briefly summarized as follows.

Table 4-3. Field Samples Collected from the Four Sites

Field Site	No. of Samples / Matrices Collected	Areas For Collecting Sample Material	Volume Required
Carson River	12 Soil 6 Sediment	Tailings Piles (Six Mile Canyon) River Bank Sediments	4 L each for soil 12 L each for sediment
Y-12	10 Sediment 6 Soil	Poplar Creek Sediments Old Mercury Recovery Bldg. Soils	12 L each for sediment 4 L each for soil
Manufacturing Site	12 Soil	Subsurface Soils	4 L each
Puget Sound	4 Sediment	High-Level Mercury (below cap) Low-Level Mercury (native material)	12 L each

Preparing Slurry Matrices

For slurries (i.e., wet sediments), the mixing steps were sufficiently thorough that the sample containers could be filled directly from the mixing vessel. There were two separate mixing steps for the slurry-type samples. Each slurry was initially mixed mechanically within the sample container (i.e., bucket) in which the sample was shipped to the SAIC GeoMechanics Laboratory. A subsample of this premixed sample was transferred to a second mixing vessel. A mechanical drill equipped with a paint mixing attachment was used to mix the subsample. As shown in Figure 4-1, slurry samples bypassed the sample riffle splitting step. To ensure all sample bottles contained the same material, the entire set of containers to be filled was submerged into the slurry as a group. The filled vials were allowed to settle for a minimum of two days, and the standing water was removed using a Pasteur pipette. The removal of the standing water from the slurry samples was the only change to the homogenization procedure between the pre-demonstration and the demonstration.

Preparing "Non-Slurry" Matrices

Soils and sediments having no excess moisture were initially mixed (Step 1) and then homogenized in the sample riffle splitter (Step 2). Prior to these steps, the material was air-dried and subsampled to reduce the volume of material to a size that was easier to handle.

As shown in Figure 4-1 (Step 1), the non-slurry subsample was manually stirred with a spoon or similar equipment until the material was visually uniform. Immediately following manual mixing, the subsample was mixed and split six times for more complete homogenization (Step 2). After the 6th and final split, the sample material was leveled to form a flattened, elongated rectangle and cut into transverse sections to fill the containers (Steps 3 and 4). After homogenization, 20-mL sample vials were filled and prepared for shipment (Step 5).

For the demonstration, the vendor analyzed 197 samples, which included replicates of up to 7 samples per sample lot. The majority of the samples distributed had concentrations within the range of the vendor's technology. Some samples had expected concentrations at or below the estimated level of detection for the vendor instruments. These samples were intended to evaluate the reported MDL and PQL and also to assess the prevalence of false positives. Field samples distributed to the vendor included sediments and soils collected from all four sites, and prepared by both the slurry and dry homogenization procedures.

The field samples were segregated into broad sample sets: low, medium, and high mercury concentrations. This gave each vendor the same general understanding of the sample to be analyzed as they would typically have for field application of their instrument.

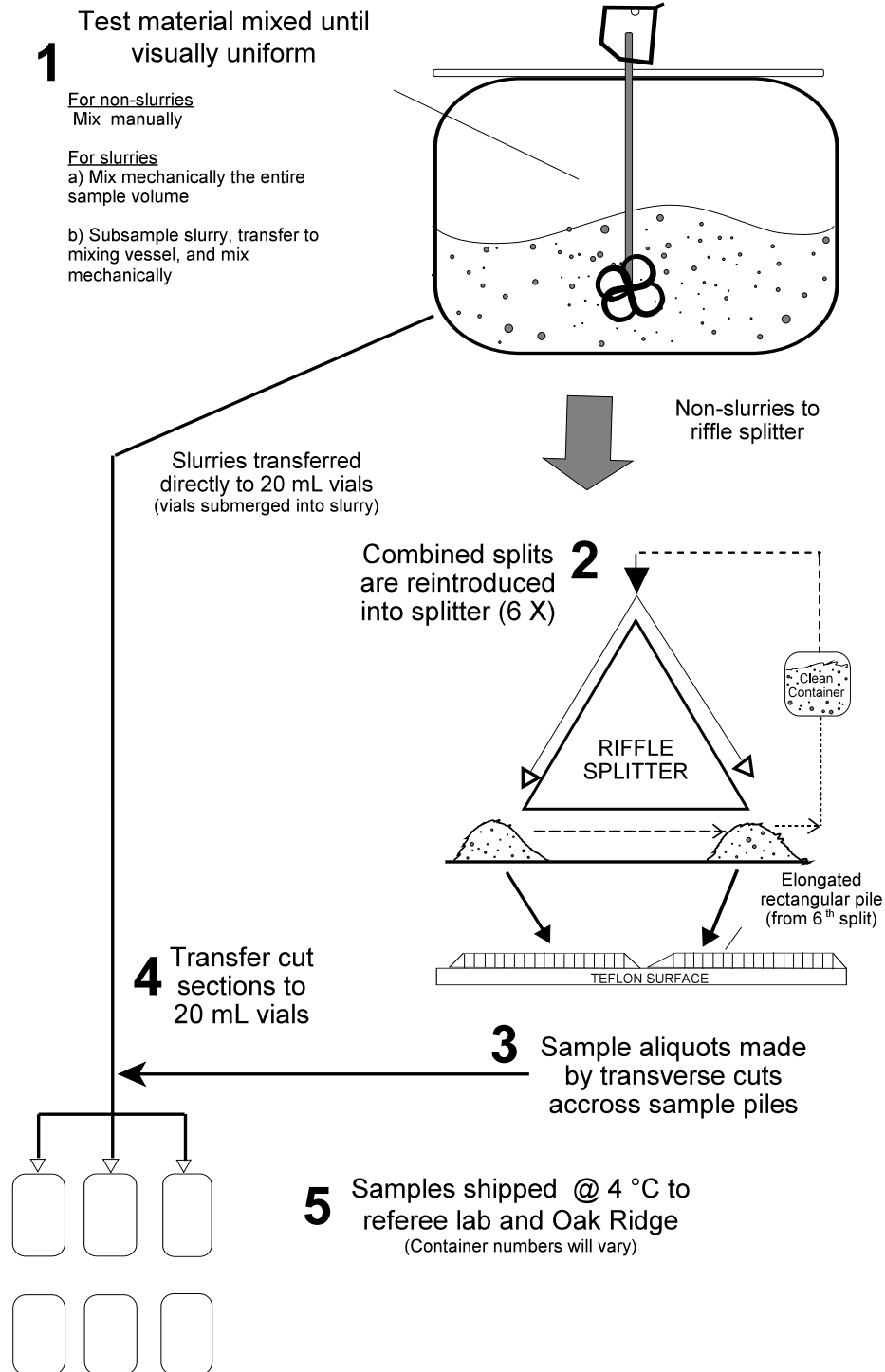


Figure 4-1. Test sample preparation at the SAIC GeoMechanics Laboratory.

In addition, selected field samples were spiked with mercury (II) chloride to generate samples with additional concentrations and to test the ability of the vendor's instrumentation to measure the additional species of mercury. Specific information regarding the vendor's sample distribution is included in Chapter 6.

4.3.1.2 Standard Reference Materials

Certified SRMs were analyzed by both the vendors and the referee laboratory. These samples were homogenized matrices which had a known concentration of mercury. Concentrations were certified values, as provided by the supplier, based on independent confirmation via multiple analyses of multiple lots and/or multiple analyses by different laboratories (i.e., round robin testing). These analytical results were then used to determine "true" values, as well as a statistically derived intervals (a 95% prediction interval) that provided a range within which the true values were expected to fall.

The SRMs selected were designed to encompass the same contaminant ranges indicated previously: low-, medium-, and high-level mercury concentrations. In addition, SRMs of varying matrices were included in the demonstration to challenge the vendor technology, as well as the referee laboratory. The referee laboratory analyzed all SRMs. SRM samples were intermingled with site field samples and labeled in the same manner as field samples.

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4.3.1.3 Spiked Field Samples

Spiked field samples were prepared by the SAIC GeoMechanics Laboratory using mercury (II) chloride. Spikes were prepared using field samples from the selected sites. Additional information was gained by preparing spikes at concentrations not previously obtainable. The SAIC GeoMechanics Laboratory's ability to prepare spikes was tested prior to the demonstration and evaluated in order to determine expected variability and accuracy of the spiked sample. The spiking procedure was evaluated by preparing several different spikes using two different spiking procedures (dry and wet). Based upon replicate analyses results, it was determined that the

wet, or slurry, procedure was the only effective method of obtaining a homogeneous spiked sample.

4.3.2 Sample Management

4.3.2.1 Sample Volumes, Containers, and Preservation

A subset from the pre-demonstration field samples was selected for use in the demonstration based on the sample's mercury concentration range and sample matrix (i.e., sediment versus soil). The SAIC GeoMechanics Laboratory prepared individual batches of field sample material to fill sample containers for each vendor. Once all containers from a field sample were filled, each container was labeled and cooled to 4 °C. Because mercury analyses were to be performed both by the vendors in the field and by the referee laboratory, adequate sample size was taken into account. Minimum sample size requirements for the vendors varied from 0.1 g or less, to 8-10 g. Only the referee laboratory analyzed separate sample aliquots for parameters other than mercury. These additional parameters included arsenic, barium, cadmium, chromium, lead, selenium, silver, copper, zinc, oil and grease, and total organic carbon (TOC). Since the mercury method (SW-846 7471B) being used by the referee laboratory requires 1 g for analysis, the sample size sent to all participants was a 20 mL vial (approximately 10 g), which ensured a sufficient volume and mass for analysis by all vendors.

4.3.2.2 Sample Labeling

The sample labeling used for the 20 mL vials consisted of an internal code developed by SAIC. This "blind" code was used throughout the entire demonstration. The only individuals who knew the key coding of the homogenized samples to the specific field samples were the SAIC TOM, the SAIC GeoMechanics Laboratory Manager, and the SAIC QA Manager.

4.3.2.3 Sample Record Keeping, Archiving, and Custody

Samples were shipped to the laboratory and the demonstration site the week prior to the demonstration. A third set of vials was archived at the SAIC GeoMechanics Laboratory as reserve samples.

The sample shipment to Oak Ridge was retained at all times in the custody of SAIC at their Oak Ridge office until arrival of the demonstration field crew. Samples were shipped under chain-of-custody (COC) and with custody seals on both the coolers and the inner plastic bags. Once the demonstration crew arrived, the coolers were retrieved

from the SAIC office. The custody seals on the plastic bags inside the cooler were broken by the vendor upon transfer.

Upon arrival at the ORNL site, the vendor set up the instrumentation at the direction and under oversight of SAIC. At the start of sample testing, the vendor was provided with a sample set representing field samples collected from a particular field site, intermingled with SRM and spiked samples. Due to variability of vendor instrument measurement ranges for mercury detection, not all vendors received samples from all the same field materials. All samples were stored in an ice cooler prior to demonstration startup and were stored in an on-site sample refrigerator during the demonstration. Each sample set was identified and distributed as a set with respect to the site from which it was collected. This was done because, in any field application, the location and general type of the samples would be known.

The vendor was responsible for analyzing all samples provided, performing any dilutions or reanalyses, as needed, calibrating the instrument if applicable, performing any necessary maintenance, and reporting all results. Any samples that were not analyzed during the day were returned to the vendor for analysis at the beginning of the next day. Once analysis of the samples from the first location were completed by the vendor, SAIC provided a set of samples from the second location. Samples were provided at the time that they were requested by the vendor. Once again, the transfer of samples was documented using a COC form.

This process was repeated for samples from each location. SAIC maintained custody of all remaining sample sets until they were transferred to the vendor. SAIC maintained custody of samples that already had been analyzed and followed the waste handling procedures in Section 4.2.2 of the Field Demonstration QAPP to dispose of these wastes.

4.4 Reference Method Confirmatory Process

The referee laboratory analyzed all samples that were analyzed by the vendor technologies in the field. The following subsections provide information on the selection of the reference method, selection of the referee laboratory, and details regarding the performance of the reference method in accordance with EPA protocols. Other parameters that were analyzed by the referee laboratory are also discussed briefly.

4.4.1 Reference Method Selection

The selection of SW-846 Method 7471B as the reference method was based on several factors, predicated on information obtained from the technology vendors, as well as the expected contaminant types and soil/sediment mercury concentrations expected in the test matrices. There are several laboratory-based, promulgated methods for the analysis of total mercury. In addition, there are several performance-based methods for the determination of various mercury species. Based on the vendor technologies, it was determined that a reference method for total mercury would be needed (Table 1-2 summarizes the methods evaluated, as identified through a review of the EPA Test Method Index and SW-846).

In selecting which of the potential methods would be suitable as a reference method, consideration was given to the following questions:

- Was the method widely used and accepted? Was the method an EPA-recommended, or similar regulatory method? The selected reference method should be sufficiently used so that it could be cited as an acceptable method for monitoring and/or permit compliance among regulatory authorities.
- Did the selected reference method provide QA/QC criteria that demonstrate acceptable performance characteristics over time?
- Was the method suitable for the species of mercury that were expected to be encountered? The reference method must be capable of determining, as total mercury, all forms of the chemical contaminant known or likely to be present in the matrices.
- Would the method achieve the necessary detection limits to evaluate the sensitivity of each vendor technology adequately?
- Was the method suitable for the concentration range that was expected in the test matrices?

Based on the above considerations, it was determined that SW-846 Method 7471B [analysis of mercury in solid samples by cold-vapor atomic absorption spectrometry (AAS)] would be the best reference method. SW-846 Method 7474, (an atomic fluorescence spectrometry method using Method 3052 for microwave digestion of the solid) had also been considered a likely technical candidate; however, because this method was not as widely used or referenced, Method 7471B was considered the better choice.

4.4.2 Referee Laboratory Selection

During the planning of the pre-demonstration phase of this project, nine laboratories were sent a statement of work (SOW) for the analysis of mercury to be performed as part of the pre-demonstration. Seven of the nine laboratories responded to the SOW with appropriate bids. Three of the seven laboratories were selected as candidate laboratories based upon technical merit, experience, and pricing. These laboratories received and analyzed blind samples and SRMs during pre-demonstration activities. The referee laboratory to be used for the demonstration was selected from these three candidate laboratories. Final selection of the referee laboratory was based upon: 1) the laboratory's interest in continuing in the demonstration, 2) the laboratory-reported SRM results, 3) the laboratory MDL for the reference method selected, 4) the precision of the laboratory calibration curve, 5) the laboratory's ability to support the demonstration (scheduling conflicts, backup instrumentation, etc.), and 6) cost.

One of the three candidate laboratories was eliminated from selection based on a technical consideration. It was determined that one of the laboratories would not be able to meet demonstration quantitation limit requirements. (Its lower calibration standard was approximately 50 µg/kg and the vendor comparison requirements were well below this value.) Two candidates thus remained, including the eventual demonstration laboratory, Analytical Laboratory Services, Inc. (ALSI):

Analytical Laboratory Services, Inc.
Ray Martrano, Laboratory Manager
34 Dogwood Lane
Middletown, PA 17057
(717) 944-5541

In order to make a final decision on selecting a referee laboratory, a preliminary audit was performed by the SAIC QA Manager at the remaining two candidate laboratories. Results of the SRM samples were compared for the two laboratories. Each laboratory analyzed each sample (there were two SRMs) in triplicate. Both laboratories were within the 95% prediction interval for each SRM. In addition, the average result from the two SRMs was compared to the 95% CI for the SRM.

Calibration curves from each laboratory were reviewed carefully. This included calibration curves generated from previously performed analyses and those generated for other laboratory clients. There were two QC requirements regarding calibration curves; the correlation coefficient had to be 0.995 or greater and the lowest point on the

calibration curve had to be within 10% of the predicted value. Both laboratories were able to achieve these two requirements for all curves reviewed and for a lower standard of 10 µg/kg, which was the lower standard required for the demonstration, based upon information received from each of the vendors. In addition, an analysis of seven standards was reviewed for MDLs. Both laboratories were able to achieve an MDL that was below 1 µg/kg.

It should be noted that vendor sensitivity claims impacted how low this lower quantitation standard should be. These claims were somewhat vague, and the actual quantitation limit each vendor could achieve was uncertain prior to the demonstration (i.e., some vendors claimed a sensitivity as low as 1 µg/kg, but it was uncertain at the time if this limit was actually a PQL or a detection limit). Therefore, it was determined that if necessary, the laboratory actually should be able to achieve even a lower PQL than 10 µg/kg.

For both laboratories, SOPs based upon SW-846 Method 7471B, were reviewed. Each SOP followed this reference method. In addition, interferences were discussed because there was some concern that organic interferences may have been present in the samples previously analyzed by the laboratories. Because these same matrices were expected to be part of the demonstration, there was some concern associated with how these interferences would be eliminated. This is discussed at the end of this subsection.

Sample throughput was somewhat important because the selected laboratory was to receive all demonstration samples at the same time (i.e., the samples were to be analyzed at the same time in order to eliminate any question of variability associated with loss of contaminant due to holding time). This meant that the laboratory would receive approximately 400 samples for analysis over the period of a few days. It was also desirable for the laboratory to produce a data report within a 21-day turnaround time for purposes of the demonstration. Both laboratories indicated that this was achievable. Instrumentation was reviewed and examined at both laboratories. Each laboratory used a Leeman mercury analyzer for analysis. One of the two laboratories had backup instrumentation in case of problems. Each laboratory indicated that its Leeman mercury analyzer was relatively new and had not been a problem in the past.

Previous SITE program experience was another factor considered as part of these pre-audits. This is because the SITE program generally requires a very high level of QC, such that most laboratories are not familiar with the QC

required unless they have previously participated in the program. A second aspect of the SITE program is that it generally requires analysis of relatively “dirty” samples and many laboratories are not used to analyzing such “dirty” samples. Both laboratories have been longtime participants in this program.

Other QC-related issues examined during the audits included 1) analyses of other SRM samples not previously examined, 2) laboratory control charts, and 3) precision and accuracy results. Each of these issues was closely examined. Also, because of the desire to increase the representativeness of the samples for the demonstration, each laboratory was asked if sample aliquot sizes could be increased to 1 g (the method requirement noted 0.2 g). Based upon previous results, both laboratories routinely increased sample size to 0.5 g, and each laboratory indicated that increasing the sample size would not be a problem. Besides these QC issues, other less tangible QA elements were examined. This included analyst experience, management involvement in the demonstration, and internal laboratory QA management. These elements were also factored into the final decision.

Selection Summary

There were very few factors that separated the quality of these two laboratories. Both were exemplary in performing mercury analyses. There were, however, some minor differences based upon this evaluation that were noted by the auditor. These were as follows:

- ALSI had backup instrumentation available. Even though neither laboratory reported any problems with its primary instrument (the Leeman mercury analyzer), ALSI did have a backup instrument in case there were problems with the primary instrument, or in the event that the laboratory needed to perform other mercury analyses during the demonstration time.
- As noted, the low standard requirement for the calibration curve was one of the QC requirements specified for this demonstration in order to ensure that a lower quantitation could be achieved. This low standard was 10 µg/kg for both laboratories. ALSI, however, was able to show experience in being able to calibrate much lower than this, using a second calibration curve. In the event that the vendor was able to analyze at concentrations as low as 1 µg/kg with precise and accurate determinations, ALSI was able to perform analyses at lower concentrations as part of the demonstration. ALSI used a second, lower calibration curve for any analyses required below 0.05

mg/kg. Very few vendors were able to analyze samples at concentrations at this low a level.

- Management practices and analyst experience were similar at both laboratories. ALSI had participated in a few more SITE demonstrations than the other laboratory, but this difference was not significant because both laboratories had proven themselves capable of handling the additional QC requirements for the SITE program. In addition, both laboratories had internal QA management procedures to provide the confidence needed to achieve SITE requirements.
- Interferences for the samples previously analyzed were discussed and data were reviewed. ALSI analyzed two separate runs for each sample. This included analyses performed with and without stannous chloride. (Stannous chloride is the reagent used to release mercury into the vapor phase for analysis. Sometimes organics can cause interferences in the vapor phase. Therefore, analysis with no stannous chloride would provide information on organic interferences.) The other laboratory did not routinely perform this analysis. Some samples were thought to contain organic interferences, based on previous sample results. The pre-demonstration results reviewed indicated that no organic interferences were present. Therefore, while this was thought to be a possible discriminator between the two laboratories in terms of analytical method performance, it became moot for the samples included in this demonstration.

The factors above were considered in the final evaluation. Because there were only minor differences in the technical factors, cost of analysis was used as the discriminating factor. (If there had been significant differences in laboratory quality, cost would not have been a factor.) ALSI was significantly lower in cost than the other laboratory. Therefore, ALSI was chosen as the referee laboratory for the demonstration.

4.4.3 Summary of Analytical Methods

4.4.3.1 Summary of Reference Method

The critical measurement for this study was the analysis of mercury in soil and sediment samples. Samples analyzed by the laboratory included field samples, spiked field samples, and SRM samples. Detailed laboratory procedures for subsampling, extraction, and analysis were provided in the SOPs included as Appendix B of the Field Demonstration QAPP. These are briefly summarized below.

Samples were analyzed for mercury using Method 7471B, a cold-vapor atomic absorption method, based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and stripped/volatilized from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an AA spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration. Potassium permanganate is added to eliminate possible interference from sulfide. As per the method, concentrations as high as 20 mg/kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water. Copper has also been reported to interfere; however, the method states that copper concentrations as high as 10 mg/kg had no effect on recovery of mercury from spiked samples. Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 254 nm. Free chlorine is removed by using an excess (25 mL) of hydroxylamine sulfate reagent. Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary analysis without reagents can determine if this type of interference is present.

Prior to analysis, the contents of the sample container are stirred and the sample mixed prior to removing an aliquot for the mercury analysis. An aliquot of soil/sediment (1 g) is placed in the bottom of a biochemical oxygen demand bottle, with reagent water and aqua regia added. The mixture is heated in a water bath at 95 °C for 2 minutes. The solution is cooled and reagent water and potassium permanganate solution are added to the sample bottle. The bottle contents are thoroughly mixed and the bottle is placed in the water bath for 30 minutes at 95 °C. After cooling, sodium chloride-hydroxylamine sulfate is added to reduce the excess permanganate. Stannous chloride is then added and the bottle attached to the analyzer; the sample is aerated and the absorbance recorded. An analysis without stannous chloride is also included as an interference check when organic contamination is

suspected. In the event of positive results of the non-stannous chloride analysis, the laboratory was to report those results to SAIC so that a determination of organic interferences could be made.

4.4.3.2 Summary of Methods for Non-Critical Measurements.

A selected set of non-critical parameters was also measured during the demonstration. These parameters were measured to provide a better insight into the chemical constituency of the field samples, including the presence of potential interferents. The results of the tests for potential interferents were reviewed to determine if a trend was apparent in the event that inaccuracy or low precision was observed. Table 4-4 presents the analytical method reference and method type for these non-critical parameters.

Table 4-4. Analytical Methods for Non-Critical Parameters

Parameter	Method Reference	Method Type
Arsenic, barium, cadmium, chromium, lead, selenium, silver, copper, zinc	SW-846 3050/6010	Acid digestion, ICP
Oil and Grease	EPA 1664	n-Hexane extraction, Gravimetric analysis
TOC	SW-846 9060	Carbonaceous analyzer
Total Solids	EPA 2540G	Gravimetric

4.5 Deviations from the Demonstration Plan

The only deviation from the demonstration Plan was that, due to a late delivery of the shipped instrument, Metorex started analyzing samples on day 2.

Chapter 5

Assessment of Laboratory Quality Control Measurements

5.1 Laboratory QA Summary

QA may be defined as a system of activities, the purpose of which is to provide assurance that defined standards of quality are met with a stated level of confidence. A QA program is a means of integrating the quality planning, quality assessment, QC, and quality improvement efforts to meet user requirements. The objective of the QA program is to reduce measurement errors to agreed-upon limits, and to produce results of acceptable and known quality. The QAPP specified the necessary guidelines to ensure that the measurement system for laboratory analysis was in control, and provided detailed information on the analytical approach to ensure that data of high quality could be obtained to achieve project objectives. The laboratory analyses were critical to project success, as the laboratory results were used as a standard for comparison to the field method results. The field methods are of unknown quality, and therefore, for comparison purposes the laboratory analysis needed to be a known quantity. The following sections provide information on the use of data quality indicators, and a detailed summary of the QC analyses associated with project objectives.

5.2 Data Quality Indicators for Mercury Analysis

To assess the quality of the data generated by the referee laboratory, two important data quality indicators of primary concern are precision and accuracy. Precision can be defined as the degree of mutual agreement of independent measurements generated through repeated application of the process under specified conditions. Accuracy is the degree of agreement of a measured value with the true or expected value. Both accuracy and precision were measured by the analysis of matrix spike/matrix spike

duplicates (MS/MSDs). The precision of the spiked duplicates is evaluated by expressing, as a percentage, the difference between results of the sample and sample duplicate results. The relative percent difference (RPD) is calculated as:

$$RPD = \frac{(\text{Maximum Value} - \text{Minimum Value})}{(\text{Maximum Value} + \text{Minimum Value})/2} \times 100$$

To determine and evaluate accuracy, known quantities of the target analytes were spiked into selected field samples. All spikes were post-digestion spikes because of the high sample concentrations encountered during the demonstration. Pre-digestion spikes, on high-concentration samples would either have been diluted or would have required additional studies to determine the effect of spiking more analyte and subsequent recovery values. To determine matrix spike recovery, and hence measure accuracy, the following equation was applied:

$$\%R = \frac{C_{ss} - C_{us}}{C_{sa}} \times 100$$

where,

C_{ss}	=	Analyte concentration in spiked sample
C_{us}	=	Analyte concentration in unspiked sample
C_{sa}	=	Analyte concentration added to sample

Laboratory control samples (LCSs) were used as an additional measure of accuracy in the event of significant

matrix interference. To determine the percent recovery of LCS analyses, the equation below was used:

$$\%R = \frac{\text{Measured Concentration}}{\text{Theoretical Concentration}} \times 100$$

While several precautions were taken to generate data of known quality through control of the measurement system, the data must also be representative of true conditions and comparable to separate sample aliquots. Representativeness refers to the degree with which analytical results accurately and precisely reflect actual conditions present at the locations chosen for sample collection. Representativeness was evaluated as part of the pre-demonstration and combined with the precision measurement in relation to sample aliquots. Sample aliquoting by the SAIC GeoMechanics Laboratory tested the ability of the procedure to produce homogeneous, representative, and comparable samples. All samples were carefully homogenized in order to ensure comparability between the laboratory and the vendor. Therefore, the RSD measurement objective of 25% or less for replicate sample lot analysis was intended to assess not only precision but representativeness and comparability.

Sensitivity was another critical factor assessed for the laboratory method of analysis. This was measured as a practical quantitation limit and was determined by the low standard on the calibration curve. Two separate calibration curves were run by the laboratory when necessary. The higher calibration curve was used for the majority of the samples and had a lower calibration limit of 25 µg/kg. The lower calibration curve was used when samples were below this lower calibration standard. The lower calibration curve had a lower limit standard of 5 µg/kg. The lower limit standard of the calibration curve was run with each sample batch as a check standard and was required to be within 10% of the true value (QAPP QC requirement). This additional check on analytical sensitivity was performed to ensure that this lower limit standard was truly representative of the instrument and method practical quantitation limit.

5.3 Conclusions and Data Quality Limitations

Critical sample data and associated QC analyses were reviewed to determine whether the data collected were of adequate quality to provide proper evaluation of the project's technical objectives. The results of this review are summarized below.

Accuracy objectives for mercury analysis by Method 7471B were assessed by the evaluation of 23 spiked duplicate pairs, analyzed in accordance with standard procedures in the same manner as the samples. Recovery values for the critical compounds were well within objectives specified in the QAPP, except for two spiked samples summarized in Table 5-1. The results of these samples, however, were only slightly outside specified limits, and given the number of total samples (46 or 23 pairs), this is an insignificant number of results that did not fall within specifications. The MS/MSD results therefore, are supportive of the overall accuracy objectives.

Table 5-1. MS/MSD Summary

Parameter	Value
QC Limits	80%- 120%
Recovery Range	85.2% - 126%
Number of Duplicate Pairs	23
Average Percent Recovery	108%
No. of Spikes Outside QC Specifications	2

An additional measure of accuracy was LCSs. These were analyzed with every sample batch (1 in 20 samples) and results are presented in Table 5-2. All results were within specifications, thereby supporting the conclusion that QC assessment met project accuracy objectives.

Table 5-2. LCS Summary

Parameter	Value
QC Limits	90%- 110%
Recovery Range	90% - 100%
Number of LCSs	24
Average Percent Recovery	95.5%
No. of LCSs Outside QC Specifications	0

Precision was assessed through the analysis of 23 duplicate spike pairs for mercury. Precision specifications were established prior to the demonstration as a RPD less

than 20%. All but two sample pairs were within specifications, as noted in Table 5-3. The results of these samples, however, were only slightly outside specified limits, and given the number of total samples (23 pairs), this is an insignificant number of results that did not fall within specifications. Therefore, laboratory analyses met precision specifications.

Table 5-3. Precision Summary

Parameter	Value
QC Limits	RPD < 20%
MS/MSD RPD Range	0.0% to 25%
Number of Duplicate Pairs	23
Average MS/MSD RPD	5.7%
No. of Pairs Outside QC Specifications	2

Sensitivity results were within specified project objectives. The sensitivity objective was evaluated as the PQL, as assessed by the low standard on the calibration curve. For the majority of samples, a calibration curve of 25-500 µg/kg was used. This is because the majority of samples fell within this calibration range (samples often required dilution). There were, however, some samples below this range and a second curve was used. The calibration range for this lower curve was 5-50 µg/kg. In order to ensure that the lower concentration on the calibration curve was a true PQL, the laboratory ran a low check standard (lowest concentration on the calibration curve) with every batch of samples. This standard was required to be within 10% of the specified value. The results of this low check standard are summarized in Table 5-4.

Table 5-4. Low Check Standards

Parameter	Value
QC Limits	Recovery 90% - 110%
Recovery Range	88.6% - 111%
Number of Check Standards Analyzed	23
Average Recovery	96%

There were a few occasions where this standard did not meet specifications. The results of these samples, however, were only slightly outside specified limits, and given the number of total samples (23), this is an insignificant number of results that did not fall within specifications. In addition, the laboratory reanalyzed the standard when specifications were not achieved, and the second determination always fell within the required limits. Therefore laboratory objectives for sensitivity were achieved according to QAPP specifications.

As noted previously, comparability and representativeness were assessed through the analysis of replicate samples. Results of these replicates are presented in the discussion on primary project objectives for precision. These results show that data were within project and QA objectives.

Completeness objectives were achieved for the project. All samples were analyzed and data were provided for 100% of the samples received by the laboratory. No sample bottles were lost or broken.

Other measures of data quality included method blanks, calibration checks, evaluation of linearity of the calibration curve, holding time specifications, and an independent standard verification included with each sample batch. These results were reviewed for every sample batch run by ALSI, and were within specifications. In addition, 10% of the reported results were checked against the raw data. Raw data were reviewed to ensure that sample results were within the calibration range of the instrument, as defined by the calibration curve. A 6-point calibration curve was generated at the start of each sample batch of 20. A few data points were found to be incorrectly reported. Recalculations were performed for these data, and any additional data points that were suspected outliers were checked to ensure correct results were reported. Very few calculation or dilution errors were found. All errors were corrected so that the appropriate data were reported.

Another measure of compliance were the non-stannous chloride runs performed by the laboratory for every sample analyzed. This was done to check for organic interference. There were no samples that were found to have any organic interference by this method. Therefore, these results met expected QC specifications and data were not qualified in any fashion.

Total solids data were also reviewed to ensure that calculations were performed appropriately and dry weights reported when required. All of these QC checks met

QAPP specifications. In summary, all data quality indicators and QC specifications were reviewed and found to be well within project specifications. Therefore, the data are considered suitable for purposes of this evaluation.

5.4 Audit Findings

The SAIC SITE QA Manager conducted audits of both field activities and of the subcontracted laboratory as part of the QA measures for this project. The results of these technical system reviews are discussed below.

The field audit resulted in no findings or non-conformances. The audit performed at the subcontract laboratory was conducted during the time of project sample analysis. One non-conformance was identified and corrective action was initiated. It was discovered that the laboratory PQL was not meeting specifications due to a reporting error. The analyst was generating the calibration curves as specified above; however, the lower limit on the calibration curve was not being reported. This was immediately rectified and no other findings or non-conformances were identified.

Chapter 6

Performance of the X-MET 2000

Metorex analysis began on May 6, 2003, analyzing 197 samples over two days as part of the demonstration conducted in Oak Ridge, TN. The demonstration started on May 5; however, due to shipping confusion the instrument was not available for analyses until May 6. Results for these samples were reported, and a statistical evaluation was performed. Additionally, the observations performed during the demonstration were reviewed, and an assessment of all primary and secondary objectives was completed. The results of the primary and secondary objectives, identified in Chapter 1, are discussed in Sections 6.1 and 6.2, respectively.

The X-MET 2000 was used during the pre-demonstration in October, 2002 and during the demonstration by Metorex personnel. During the pre-demonstration, Metorex requested soil material from each of the sampling sites to enable the development of matrix-matched calibration curves. Soil samples were therefore sent to Metorex from Carson River, the Manufacturing Site, and Oak Ridge. Due

to the limited number of Puget Sound samples, soil was not sent from Puget Sound as part of this pre-demonstration effort. Hence, matrix matched Puget Sound calibration standards were not available for sample analysis. The approximate concentrations for the soil from Carson River were 8, 150, and 850 mg/kg. The approximate concentrations for the soil from the manufacturing site were 6, 55, 282, 490, and 774 mg/kg. The approximate concentrations for the soil from Oak Ridge were 10, 96, 210, and 420 mg/kg. Determining the exact mercury concentration of the soil material; however, was the responsibility of Metorex.

The distribution of the samples prepared for Metorex and the referee laboratory is presented in Table 6-1. From the four sites, Metorex received samples at 35 different concentrations for a total of 197 samples. These 197 samples consisted of 23 concentrations in replicates of 7, and 12 concentrations in replicates of 3.

Table 6-1. Distribution of Samples Prepared for Metorex and the Referee Laboratory

Site	Concentration Range	Sample Type			SRM
		Soil	Sediment	Spiked Soil	
Carson River (Subtotal = 30)	Low (1-500 ppb)	0	0	0	0
	Mid (0.5-50 ppm)	9	0	0	0
	High (50->1,000 ppm)	0	0	7	14
Puget Sound (Subtotal = 34)	Low (1 ppb - 10 ppm)	3	0	0	0
	High (10-500 ppm)	0	10	7	14
Oak Ridge (Subtotal = 58)	Low (0.1-10 ppm)	0	7	0	0
	High (10-800 ppm)	13	10	14	14
Manufacturing (Subtotal = 75)	General (5-1,000 ppm)	33	0	14	28
Subtotal (Total = 197)		58	27	42	70

6.1 Primary Objectives

6.1.1 Sensitivity

Sensitivity objectives are explained in Chapter 4. The two primary sensitivity evaluations performed for this demonstration were the MDL and PQL. Determinations of these two measurements are explained in the paragraphs below, along with a comparison to the referee laboratory. These determinations set the standard for the evaluation of accuracy and precision for the Metorex field instrument. Any sample analyzed by Metorex and subsequently reported as below their level of detection was not used as part of any additional evaluations. This was done because of the expectation that values below the lower limit of instrument sensitivity would not reflect the true instrument accuracy and precision.

The sensitivity measurements of MDL and PQL are both dependent upon the matrix and method. Hence, the MDL and PQL will vary, depending upon whether the matrix is a soil, waste, or water. Only soils and sediments were tested during this demonstration and therefore, MDL calculations for this evaluation reflect soil and sediment matrices. PQL determinations are not independent calculations, but are dependent upon results provided by the vendor for the samples tested.

Comparison of the MDL and PQL to laboratory sensitivity required that a standard evaluation be performed for all instruments tested during this demonstration. PQL, as previously noted, is defined in EPA G-5i as the lowest level of method and instrument performance with a specified accuracy and precision. This is often defined by the lowest point on the calibration curve. Because the Metorex field instrument does not use a calibration curve for the analysis of samples, but instead depends upon instrument counts and an associated standard deviation to determine the lower level of quantitation, our approach was to let the vendor provide the lower limits of quantitation as determined by their particular standard operating procedure, and then test these limits by comparing results to the referee laboratory results, or comparing the results to a standard reference material, if available. Comparison of these data are, therefore, presented for the lowest level sample results, as provided by the vendor. In other words, if Metorex provided “non detect” data for specific samples, then no formal evaluation of that sample was presented. In addition, that sample (or samples) was not used in the evaluation of precision and accuracy.

Method Detection Limit – The standard procedure for determining MDLs is to analyze a low standard or

reference material seven times, calculate the standard deviation and multiply the standard deviation by the “t” value for seven measurements at the 99th percentile ($\alpha = 0.01$). (This value is 3.143, as determined from a standard statistics table.) This procedure for determination of an MDL is defined in 40 CFR Part 136, and while determinations for MDLs may be defined differently for other instruments, this method was previously noted in the demonstration QAPP and is intended to provide a comparison to other similar MDL evaluations. The purpose is to provide a lower level of detection with a statistical confidence at which the instrument will detect the presence of a substance above its noise level. There is no associated accuracy or precision provided or implied.

Several blind standards and field samples were provided to Metorex at their estimated lower limit of sensitivity. The Metorex lower limit of sensitivity was previously estimated at 10 mg/kg. Because there are several different SRMs and field samples at concentrations close to the MDL, evaluation of the MDL was performed using more than a single concentration. Samples chosen for calculation were based upon: 1) concentration and how close it was to the estimated MDL, 2) number of analyses performed for the same sample (e.g., more than 4), and 3) if non-detects were reported by Metorex for a sample used to calculate the MDL. Then the next highest concentration sample was selected based upon the premise that a non-detect result reported for one of several samples indicates the selected sample is on the “edge” of the instruments detection capability.

Seven replicates were analyzed by Metorex for a sample that had a reported average concentration by the referee laboratory of 10.5 mg/kg. (Sample lot 17 from the Manufacturing site.) The average concentration reported by Metorex for this sample was 49.3 mg/kg, and the standard deviation was 8.56 mg/kg. An SRM with a reference value of 6.56 mg/kg (sample lot 45 from the manufacturing site) was analyzed seven times by Metorex, with a reported average concentration of 76.7 mg/kg and a standard deviation of 5.25 mg/kg. Calculations of the respective MDLs based upon each of these standards is 26.9 and 16.5 mg/kg.

As a further check of the MDL, sample lot 14 from the Oak Ridge samples had a reported concentration of 4.74 mg/kg by the referee laboratory. All samples analyzed by Metorex for this sample are reported as “non-detect” or estimated. Sample lot 21 had a reported concentration of 11.2 mg/kg by the referee laboratory. This sample was analyzed only three times by Metorex, with all but one result reported as

estimated values. The one exception was reported at 22 mg/kg. Therefore, it appears that this sample is right on the edge of the instrument's capability for reporting between a non-detect and a detected value.

Based upon the results presented above, it appears that the MDL for this instrument is close to 11 mg/kg. (Sample results from sample lot 21 perhaps provide the best evidence for the instrument MDL.) The range for the calculated MDL is between 16.5 and 26.9 mg/kg, based on the results of seven replicates for low standards or samples, as shown above.

There may be, however, some inherent matrix differences between these samples, and hence the reason for values provided by Metorex for the SRM with a concentration of 6.56 mg/kg. The equivalent MDL for the referee laboratory is 0.0026 mg/kg. The calculated result is also only intended as a statistical estimation, and not a true test of instrument sensitivity. The estimated sensitivity provided by Metorex of 10 mg/kg is a reasonable estimation of the MDL, assuming that some samples will likely have matrix interferences, and therefore may result in a slightly higher MDL as estimated for soils and/or sediments.

Practical Quantitation Limit – This value is usually calculated by determining a low standard on the instrument calibration curve, and it is estimated as the lowest standard at which the instrument will accurately and precisely determine a given concentration within specified QC limits. For the Metorex field instrument, there is no calibration curve, and therefore the low standard from a calibration curve is not a valid estimation of the PQL. The PQL is often around 5-10 times the MDL. This PQL estimation, however, is method- and matrix-dependent. In order to determine the PQL, several low standards were provided to Metorex and subsequent %Ds were calculated.

The lower limit of sensitivity previously provided by the vendor (10 mg/kg) appears to be close to their MDL, but this would likely result in a higher instrument and method PQL. The relationship between sensitivity and precision is such that the lower the concentration, the higher the variation in reported sample results. The PQL should have a precision and accuracy that matches the instrument capabilities within a certain operating range of analysis and therefore, the following data were reviewed.

The result for the 11.2 mg/kg sample noted above (sample lot 21) had two estimated and one actual reported value by Metorex and therefore this sample was not used for determination of the PQL. It also appears to be close to the instrument MDL, and therefore this concentration would

seem to be lower than the Metorex field instrument could accurately and precisely determine.

Five times the estimated MDL would result in a value of 55-135 mg/kg. Therefore, values in this range were chosen for estimating the PQL and associated %D between the Metorex reported average and the reference value, if it is an SRM, or the average value reported by the referee laboratory. Also compared are the 95% CI for additional descriptive information. In addition, values below the estimated value of 55 mg/kg are included to determine if the instrument capabilities can provide an even lower PQL.

Sample lot 19 (Manufacturing Site) has an average value of 28.7 mg/kg reported by the referee laboratory and a standard deviation of 9.24 mg/kg. The 95% CI for this sample is 20.2 to 37.2 mg/kg. The Metorex average value is 61.0 mg/kg, which is outside the range of the 95% CI. The %D between this value and the referee laboratory is 113%.

Sample lot 27 (Puget Sound) has an average value of 45.7 mg/kg reported by the referee laboratory, and a standard deviation of 10.2 mg/kg. The 95% CI for this sample is 36.3 to 55.1 mg/kg. The Metorex average value is 177 mg/kg which is outside the range of the 95% CI. The %D between this value and the referee laboratory is 287%.

Sample lot 65 (Oak Ridge) has an average value of 62.9 mg/kg reported by the referee laboratory, and a standard deviation of 8.48 mg/kg. The 95% CI for this sample is 55.1 to 70.7 mg/kg. The Metorex average value is 91.3 mg/kg which is outside the range of the 95% CI. The %D between this value and the referee laboratory is 45.2%.

Sample lot 20 (manufacturing site) has an average value of 63.9 mg/kg reported by the referee laboratory, and a standard deviation of 16.2 mg/kg. The 95% CI for this sample is 48.9 to 78.9 mg/kg. The Metorex average value is 75.4 mg/kg which is within the range of the 95% CI. The %D between this value and the referee laboratory is 18.0%.

Sample lot 48 (SRM) has a reference value of 77.8 mg/kg, with a 95% CI of 71.5 to 84.0 mg/kg. The Metorex average value is 189 mg/kg, which is outside the range of the 95% CI. The %D between this value and the reference value is 143%. The referee laboratory result for this SRM (sample lot 48) is 87.1 mg/kg, which is just outside the 95% CI. The %D between this value and the reference value is 12.0%.

It could be suggested that the Metorex field instrument PQL is approximately 64 mg/kg, based on the results presented above with the %D reported as 18%.

Sensitivity Summary – The low standard calculations suggest that a PQL for the Metorex field instrument may be somewhere around 64 mg/kg. The referee laboratory PQL confirmed during the demonstration is 0.005 mg/kg. The %D for the average Metorex result for the SRM value of 77.8 mg/kg, however, is extremely high. In addition, as noted in Section 6.1.2, Metorex results are inaccurate even at higher concentrations. Therefore, given the definition associated with a PQL with a defined accuracy and precision, an actual PQL for the Metorex field instrument is difficult to define. The range for the calculated MDL is between 16.5 and 26.9 mg/kg, based on the results of seven replicate analyses for low standards. The MDL determination, however, is only a statistical calculation that has been used in the past by EPA, and is currently not considered a “true” MDL by SW-846 methodology. SW-846 is suggesting that performance-based methods be used, and that PQLs be determined using low standard calculations. The equivalent MDL for the referee laboratory is 0.0026 mg/kg.

6.1.2 Accuracy

Accuracy is the instrument measurement compared to a standard or true value. For this demonstration, three separate standards were used for determining accuracy. The primary standard is SRMs. The SRMs are traceable to national systems. These were obtained from reputable suppliers with reported concentration and associated 95% CI and 95% prediction interval. The CI from the reference material is used as a measure of comparison with the CI calculated from replicate analyses for the same sample analyzed by the laboratory or vendor. Results are considered comparable if CIs of the SRM overlap with the CIs computed from the replicate analyses.

Prediction intervals are intended as a measure of comparison for a single laboratory or vendor result with the SRM. When computing a prediction interval, the equation assumes an infinite number of analyses, and is it used to compare individual sample results. A 95% prediction interval would, therefore, predict the correct result from a single analysis 95% of the time for an infinite number of samples, if the result is comparable to that of the SRM. It should be noted that the corollary to this statement is that 5% of the time a result will be outside the prediction interval if determined for an infinite number of samples. If several samples are analyzed, the percentage of results within the prediction interval will be slightly above or below 95%. The more samples analyzed, the more likely the percentage of correct results will be close to 95% if the result for the method being tested is comparable to the SRM.

All SRMs were analyzed in replicates of seven by both the vendor and by the referee laboratory. There were 10 SRM sample lots; however, 1 of the 10 SRM sample lots was not used in the comparison, due to the disparity of the results obtained by both the vendor and referee laboratory, and the continued disparity of these results upon reanalysis by the referee laboratory. Apparently, this SRM was an anomaly and did not provide accurate information for comparison. Therefore, there were 9 different SRM sample lots analyzed by both the vendor and the laboratory for a total of 63 analyses used for comparison.

The second accuracy determination used a comparison of vendor results of field samples and SRMs to the referee laboratory results for these same samples. Field samples were used to ensure that “real-world” samples were tested by the vendor. The referee laboratory result is considered as the standard for comparison to the vendor result. This comparison is in the form of a hypothesis test with $\alpha = 0.01$. (Detailed equations along with additional information about this statistical comparison is included in Appendix B.)

It should be noted that there is evidence of a laboratory bias. This bias was determined by comparing average laboratory values to SRM reference values and is discussed below. The laboratory bias is low in comparison to the reference value. A bias correction was not made when comparing individual samples (replicate analyses) between the laboratory and vendor; however, setting $\alpha = 0.01$ helps mitigate for this possible bias by widening the range of acceptable results between the two data sets.

An aggregate analysis, or unified hypothesis test, was also performed for all 32 sample lots. (A detailed discussion of this statistical comparison is included in Appendix B.) This analysis provides additional statistical evidence in relation to the accuracy evaluation. A bias term is included in this calculation in order to account for any data bias.

The third measure of accuracy is obtained by the analysis of spiked field samples. These were analyzed by the vendor and the referee laboratory in replicate in order to provide additional measurement comparisons and are treated the same as field samples. Spikes were prepared to cover additional concentrations not available from SRMs or field samples. There is no comparison to the spiked concentration; only a comparison between the vendor and the laboratory reported value.

The purpose for SRM analysis by the referee laboratory is to provide a check on laboratory accuracy. During the pre-demonstration, the referee laboratory was chosen, in part, based upon the analysis of SRMs. This was done in

order to ensure that a competent laboratory would be used for the demonstration. The pre-demonstration laboratory qualification showed that the laboratory was within prediction intervals for all SRMs analyzed. Because of the need to provide confidence in laboratory analysis during the demonstration, the referee laboratory also analyzed SRMs as an ongoing check on laboratory bias. As noted in Table 6-3, not all laboratory results were within the prediction interval. This is discussed in more detail below. All laboratory QC checks, however, were found to be within compliance (see Chapter 5).

Evaluation of vendor and laboratory analysis of SRMs is performed in the following manner. Accuracy was

determined by comparing the 95% CI of the sample analyzed by the vendor and laboratory to the 95% CI for the SRM. (95% CIs around the true value are provided by the SRM supplier.) This is provided in Tables 6-2 and 6-3, with notations when the CIs overlap, suggesting comparable results. In addition, the number of SRM results for the vendor's analytical instrumentation and the referee laboratory that are within the associated 95% prediction interval are reported. This is a more definitive evaluation of laboratory and vendor accuracy. The percentage of total results within the prediction interval for the vendor and laboratory are reported in Tables 6-2 and 6-3, respectively.

Table 6-2. Metorex SRM Comparison

Sample Lot No.	SRM Value/ 95% CI	Metorex Avg./ 95% CI	CI Overlap (yes/no)	No. of Samples Analyzed	95% Prediction Interval	Metorex No. w/in Prediction Interval
51	405 / 365 - 445 ^a	126 / 122 - 129	no	7	194 - 615	0
48	77.8 / 71.5 - 84.0	189 / 180 - 198	no	7	45.6 - 110	0
50	203 / 183 - 223 ^a	254 / 172 - 336	yes	7	97.4 - 308	4
53	910 / 820 - 1000 ^a	419 / 408 - 430	no	7	437 - 1380	1
54	1120 / 1020 - 1220 ^a	509 / 496 - 522	no	7	582 - 1700	0
45	6.45 / 6.06 - 6.84	76.7 / 71.8 - 81.6	no	7	4.83 - 8.06	0
47	32.6 / 32.3 - 32.9 ^a	176 / 166 - 186	no	7	30.8 - 34.4	0
49	99.8 / 81.9 - 118	181 / 174 - 188	no	7	31.3 - 168	1
52	608 / 548 - 668 ^a	299 / 289 - 309	no	7	292 - 924	6
Total Samples				63		12
% of samples w/in prediction interval						19%

a CI is estimated based upon n=30. A 95% prediction interval was provided by the SRM supplier, but no CI was given.

Table 6-3. ALSI SRM Comparison

Sample Lot No.	SRM Value/ 95% CI	ALSI Avg./ 95% CI	CI Overlap (yes/no)	No. of Samples Analyzed	95% Prediction Interval	ALSI No. w/in Prediction Interval
51	405 / 365 - 445 ^a	291 / 255 - 327	no	7	194 - 615	7
48	77.8 / 71.5 - 84.0	87.1 / 57.0 - 117	yes	6	45.6 - 110	4
50	203 / 183 - 223 ^a	167 / 140 - 194	yes	7	97.4 - 308	7
53	910 / 820 - 1000 ^a	484 / 325 - 643	no	7	437 - 1380	4
54	1120 / 1020 - 1220 ^a	711 / 573 - 849	no	7	582 - 1700	5
45	6.45 / 6.06 - 6.84	5.44 / 4.10 - 6.78	yes	6	4.83 - 8.06	5
47	32.6 / 32.3 - 32.9 ^a	20.5 / 15.4 - 25.6	no	7	30.8 - 34.4	0
49	99.8 / 81.9 - 118	84.2 / 74.5 - 93.9	yes	7	31.3 - 168	7
52	608 / 548 - 668 ^a	424 / 338 - 510	no	7	292 - 924	6
Total Samples				61		45
% of samples w/in prediction interval						74%

a CI is estimated based upon n=30. A 95% prediction interval was provided by the SRM supplier but no CI was given.

The single most important number from these tables is the percentage of samples within the 95% prediction interval. As noted for the Metorex data, this percentage is 19%, with

n = 63. As seen from the tabulated data, average results fall both above and below the reference value. This would suggest that there is no particular bias. There is also no

concentration correlation with the results. In determining the number of results significantly above or below the reference value, 8 of 9 average results are greater than 50% different. This suggests that the numbers reported by Metorex fluctuate well outside SRM values.

For a single value (as will be noted in the section discussing precision), sample results are generally within a very narrow range. Therefore, it is apparently not scatter or random variation that causes sample results to be outside reference values. It is more likely some type of matrix interference. In some instances, this is a positive interference and other instances, this is a negative interference. More discussion on interference will be presented in the section below which presents the results of the hypothesis tests. These test results compare the vendor to the referee laboratory for each of the four matrices tested.

The percentage of samples within the 95% prediction interval for the referee laboratory data is 74%, with $n = 61$. For 8 of the 9 different SRMs, ALSI average results are below the reference value. This would suggest that the ALSI data are potentially biased low. Because of this bias, the percentage of samples outside the prediction interval is below the anticipated number of results, given that the number of samples analyzed (61) is relatively high. Note also that the SRM reference value for sample lot number 47 has a very narrow prediction interval. This seemed unusual, but was verified with the supplier information. Nonetheless, the referee laboratory data should be considered accurate when one corrects for bias as is done in the aggregate analysis. Because there is no bias correction term in the individual hypothesis tests, α is set at 0.01 to help mitigate for this laboratory bias. This in effect widens the scope of vendor data that would fall within an acceptable range of the referee laboratory. (The α is set at 0.05 for the SRM prediction intervals by the SRM supplier.)

Hypothesis Testing

Sample results from field and spiked field samples for the vendor compared to similar tests by the referee laboratory are used as another accuracy check. Spiked samples were used to cover concentrations not found in the field samples, and they are considered the same as the field samples for purposes of comparison. Because of the limited data available for determining the accuracy of the spiked value, these were not considered the same as reference standards. Therefore, these samples were

evaluated in the same fashion as field samples, but they were not compared to individual spiked concentrations.

Using a hypothesis test with $\alpha = 0.01$, vendor results for all sample lots were compared to laboratory results to determine if sample populations are the same or significantly different. This was performed for each sample lot separately. Because this test does not separate precision from bias, if Metorex's or ALSI's computed standard deviation was large due to a highly variable result (indication of poor precision), the two CIs could overlap. Therefore, the fact that there was no significant difference between the two results would likely be due to high sample variability. Poor precision therefore, increases the likelihood that two different sample populations will be considered statistically the same. However, overall precision, as noted from the precision evaluation (Section 6.1.3), is within expected ranges for both Metorex and ALSI data. Accordingly, associated RSDs have also been reported in Table 6-4 along with results of the hypothesis testing for each sample lot.

Of the 32 sample lots, 22 results are significantly different per the previously cited hypothesis test. This number suggests that the vendor results were not comparable to the referee laboratory. There were no apparent patterns to these differences. All Metorex results with concentrations at 45.7 mg/kg or below (see sample group 27) were statistically different from the laboratory results. Sample group 20 with a concentration of 63.9 mg/kg was considered statistically the same as the laboratory. This would suggest a possible quantitation limit between 45.7 and 63.9 mg/kg (see Section 6.1.1). The PQL, however, was difficult to determine given the differences noted between Metorex values and SRM reference values or referee laboratory results.

As previously noted average results for Metorex appear evenly split between being higher and lower than the referee laboratory result. Based on the RPD calculation (Metorex to ALSI), there are 18 positive results and 14 negative results. Because the ALSI data is potentially biased low, there would be an expectation of more positive than negative results; however, the difference noted above is not enough to suggest a positive or negative bias for the Metorex data. The Metorex to SRM results confirm that no specific pattern is present. The number of average results reported by Metorex below the SRM value is 4 and the number of average results above the SRM value is 5.

Table 6-4. Accuracy Evaluation by Hypothesis Testing

Sample Lot No./ Site	Avg. Conc. mg/kg	RSD or CV	Number of Measurements	Significantly Different at Alpha = 0.01	Relative Percent Difference (Metorex to ALSI)
22/ Oak Ridge					
Metorex	57.0	21.1%	3		
ALSI	81.6	9.4%	3	no	-35.5%
24/ Oak Ridge					
Metorex	119	19.9%	7		
ALSI	207	48.4%	7	no	-54.0%
26/ Oak Ridge					
Metorex	143	46.6%	7		
ALSI	77.0	13.2%	7	no	60.0%
31/ Oak Ridge					
Metorex	427	0.89%	3		
ALSI	947	13.2%	3	no	-75.6%
51/ Oak Ridge					
Metorex	126	3.0%	7		
ALSI	291	13.4%	7	yes	-79.1%
65/ Oak Ridge					
Metorex	91.3	13.0%	7		
ALSI	62.9	13.5%	7	yes	36.8%
67/ Oak Ridge					
Metorex	492	4.3%	7		
ALSI	835	14.8%	7	yes	-51.7%
11/ Puget Sound					
Metorex	29.3	13.8%	3		
ALSI	0.81	32.7%	7	yes	189%
25/ Puget Sound					
Metorex	137	4.0%	3		
ALSI	16.6	12.3%	3	yes	157%
27/ Puget Sound					
Metorex	177	12.8%	7		
ALSI	45.7	22.2%	7	yes	118%
48/ Puget Sound					
Metorex	189	5.4%	7		
ALSI	87.1	32.9%	7	yes	73.8%
50/ Puget Sound					
Metorex	254	35.0%	7		
ALSI	167	17.7%	7	no	41.3%
62/ Puget Sound					
Metorex	76.7	7.2%	7		
ALSI	14.6	28.3%	7	yes	136%
15/ Carson River					
Metorex	46.7	10.8%	3		
ALSI	4.2	24.5%	7	yes	167%
16/ Carson River					
Metorex	52.3	12.1%	3		
ALSI	7.1	13.7%	3	yes	152%
18/ Carson River					
Metorex	44.0	8.2%	3		
ALSI	10.1	8.0%	7	yes	125%
53/ Carson River					
Metorex	419	2.8%	7		
ALSI	484	35.5%	7	no	-14.4%
54/ Carson River					
Metorex	509	2.9%	7		
ALSI	711	21.0%	7	no	-33.1%
63/ Carson River					
Metorex	159	4.8%	7		
ALSI	169	6.6%	7	no	-6.1%

Table 6-4. Continued

Sample Lot No./ Site	Avg. Conc. mg/kg	RSD or CV	Number of Measurements	Significantly Different at Alpha = 0.01	Relative Percent Difference (Metorex to ALSI)
13/ Manufacturing Site					
Metorex	49.0	5.4%	3	yes	157%
ALSI	5.9	15.4%	7		
17/ Manufacturing Site				yes	130%
Metorex	49.3	17.4%	7		
ALSI	10.5	14.6%	7		
19/ Manufacturing Site				yes	72.0%
Metorex	61.0	10.2%	3		
ALSI	28.7	32.2%	7		
20/ Manufacturing Site				no	16.5%
Metorex	75.4	10.9%	7		
ALSI	63.9	25.4%	7		
29/ Manufacturing Site				yes	-62.0 %
Metorex	197	6.6%	3		
ALSI	374	17.4%	7		
32/ Manufacturing Site				yes	-93.1 %
Metorex	216	5.8%	3		
ALSI	592	12.7%	7		
33/ Manufacturing Site				yes	-126%
Metorex	273	9.1%	7		
ALSI	1204	13.3%	7		
45/ Manufacturing Site				yes	174%
Metorex	76.7	6.8%	7		
ALSI	5.4	23.4%	7		
47/ Manufacturing Site				yes	158%
Metorex	176	6.2%	7		
ALSI	20.5	27.0%	7		
49/ Manufacturing Site				yes	73.0%
Metorex	181	4.1%	7		
ALSI	84.2	12.8%	7		
52/ Manufacturing Site				no	-34.6%
Metorex	299	3.4%	7		
ALSI	424	21.9%	7		
64/ Manufacturing Site				yes	-16.3%
Metorex	242	2.6%	7		
ALSI	285	8.9%	7		
66/ Manufacturing Site				yes	-48.3%
Metorex	545	3.7%	7		
ALSI	892	11.2%	7		

CV = Coefficient of variance

In determining the number of results significantly above or below the value reported by the referee laboratory, 22 of 32 average results are greater than 50% different. The %D is

further specified in Table 6-5. This suggests that the numbers reported by Metorex fluctuate well outside results reported by the referee laboratory.

Table 6-5. Number of Samples Within Each %D Range

	<30%	>30%, <50%	>50%, <100%	>100%	Total
Positive %D	1	2	4	11	18
Negative %D	3	4	6	1	14
Total	4	6	10	12	32

In addition to the statistical summary presented above, data plots (Figures 6-1 and 6-2) are included in order to present a visual interpretation of the accuracy. Two separate plots have been included for the Metorex data.

These two plots are divided based upon sample concentration in order to provide a more detailed presentation. Concentrations of samples analyzed by Metorex ranged approximately from 1-900 mg/kg.

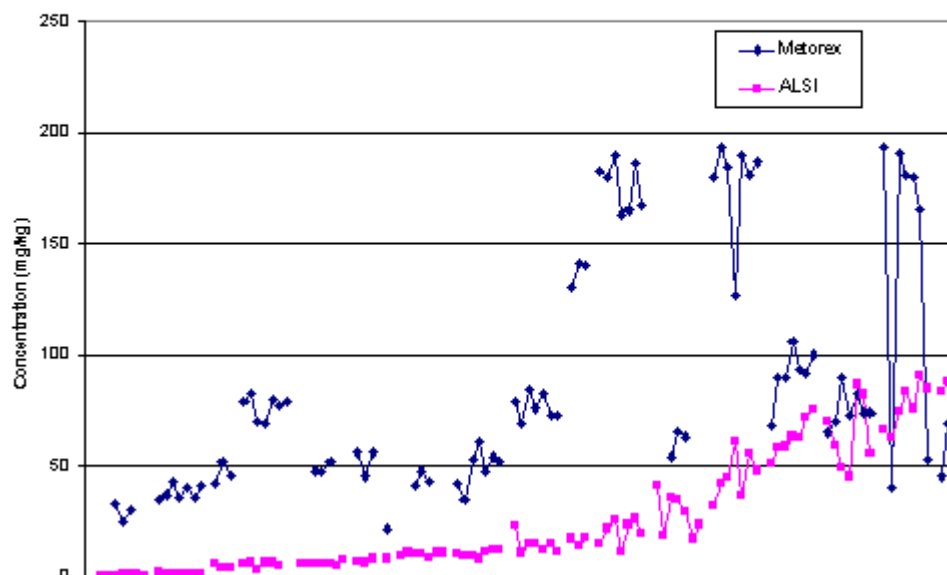


Figure 6-1. Data plot for low concentration sample results.

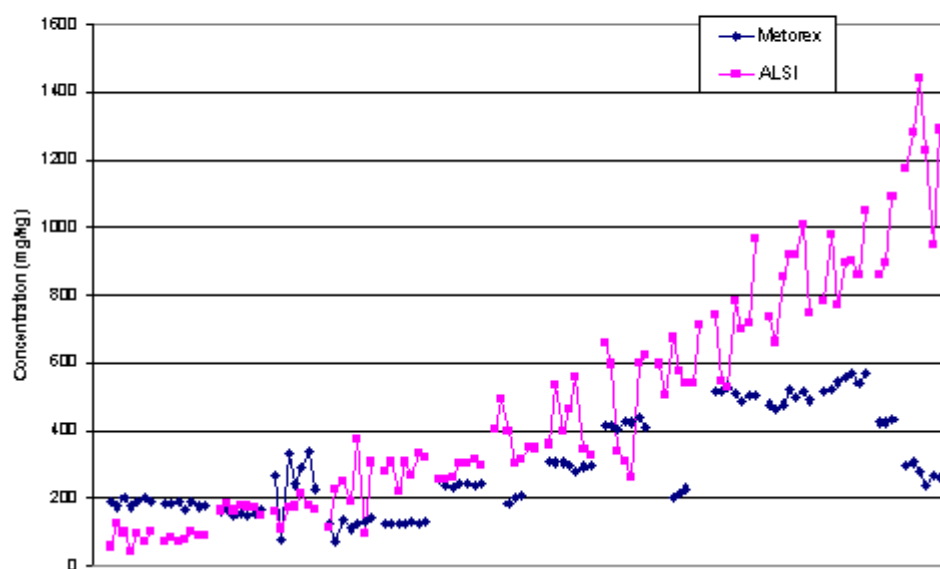


Figure 6-2. Data plot for high concentration sample results.

The previous statistical summary eliminated some of these data based upon whether concentrations were interpreted to be in the analytical range of the Metorex field instrument. This graphical presentation presents all data points. It shows Metorex data compared to ALSI data plotted against concentration. Sample groups are shown by connecting lines. Breaks between groups indicate a different set of samples at a different concentration. Sample groups were arranged from lowest to highest concentration.

As can be seen by this presentation, samples analyzed by Metorex below about 100 mg/kg did not match well with the ALSI results. For concentrations, from 200-400 mg/kg, sample results were much closer to ALSI with some deviations present. Concentrations above 400 mg/kg also appear to be different from the ALSI results. This is only a visual interpretation and does not provide statistical significance. It does, however, provide a visual interpretation that supports the previous statistical results for accuracy, as presented above.

Discussion of Interferences

The RSDs for Metorex are small, suggesting that precision is good, and the differences noted above are not simply the result of random variation. (This will be discussed in more detail in Section 6.1.3) As noted previously, it appears that interference is the cause of the inaccurate analyses, but it is not readily apparent as to the interferent causing the problem. Specifically, there is no apparent significant difference between reported values and associated sites from which the samples were collected. There are possible exceptions, however, noted for the Oak Ridge and Puget Sound samples, but these are only descriptive observations. For example, discounting SRMs, for the Oak Ridge site, 4 of the 5 results reported by Metorex are not statistically different from the referee laboratory results. There also appears to be more significant differences in the Puget Sound sample set than any of the other sample lots, where only 1 of the 4 sample sets are considered the same as the laboratory, again eliminating SRM results. Therefore, there may be a significant interference in the Puget Sound samples not present in the Carson River samples. This is further supported by the fact that soil for matrix matched calibration standards was supplied for the Carson River site, and not for the Puget Sound site.

Upon examination of additional data collected for these samples (see Table 6-6), no apparent differences were noted, as was no apparent difference noted for the higher match with the Oak Ridge samples. For example, a high organic content may cause interference, but not all the Puget Sound samples necessarily have a higher organic

content than other samples tested. In addition, the Method 7471B mercury analysis requires that a non-stannous chloride analysis be conducted with each sample analyzed, in order to test for organic interferences. Upon examination of the referee laboratory data for the sample sets mentioned above, there was no apparent interference noted in the non-stannous chloride analyses.

Puget Sound samples also had a higher percentage of moisture for some of the samples analyzed which may help explain these differences. But this does not explain all differences or all similarities. There are not enough samples to suggest that this difference is statistically significant. Other interferences caused by additional elements were also not found to be significant. A review of the analyte data presented in Table 6-6 did not identify any trends that might point to the potential cause of the impact on the accuracy. A review of the ratio of total metal concentration to the mercury concentration, however, did provide evidence of a trend. (This ratio was obtained by adding together the concentration of the metals analyzed, and dividing by the average concentration of the mercury present in the sample.) When the ratio of total metal:mercury was greater than 10, the hypothesis test (Table 6-4) indicated that for 11 of 11 sample lots the X-MET 2000 and referee laboratory results were significantly different. When the ratio of total metal:mercury was less than 10, the hypothesis test (Table 6-4) indicated that for 10 of 20 sample lots the X-MET 2000 and referee laboratory results were significantly different. No further correlation was identified when the ratio was less than 10:1.

Of course, there could be interferences that were not tested, and therefore, while it may be an interference (or likely a combination of interferences) particular to a sample lot, the exact cause remains unknown. The reason(s) for these similarities and differences and the reason(s) for the difference between the Metorex and referee laboratory results is only speculative.

Unified Hypothesis Test

SAIC performed a unified hypothesis test analysis to assess the comparability of analytical results provided by Metorex and those provided by ALSI. (See Appendix B for a detailed description of the Test.) Metorex and ALSI both supplied multiple assays on replicates derived from a total of 33 different sample lots, both field materials and SRMs. The other two sample lots were excluded because there were not a sufficient number of reported results above the Metorex detection limit. The Metorex and ALSI data from these assays formed the basis of this assessment.

The null hypothesis tested was that, on average, Metorex and ALSI produce the same results within a given sample lot. The null hypothesis is rejected and the two sample sets were therefore considered to be different. Additionally, a bias term was incorporated into the analysis to account for the laboratory "low" bias and the null hypothesis was still rejected, indicating the disagreement between the Metorex

and ALSI analytical results. Furthermore, a review of the statistical analysis details that the overall discordance between Metorex and ALSI analytical results cannot be traced to the disagreement in results for one or two sample lots. Additional information about this statistical evaluation is included in Appendix B.

Table 6-6. Concentration (in mg/kg) of Non-Target Analytes

Lot #	Site	TOC	O&G	Ag	As	Ba	Cd	Cr	Cu	Pb	Se	Sn	Zn	Hg
1	Carson River	870	190	<0.5	9	210	<0.5	19	13	3	<2	<5	60	0.19
11	Puget Sound	3800	130	<0.5	4	20	<0.5	18	8	1	<2	<5	24	0.63
13	Manufacturing Site	3200	100	<0.5	2	110	<0.5	42	51	7	<2	<5	61	5.5
14	Oak Ridge	7800	180	0.32	2	41	0.4	16	9	11	<2	<4	74	78
15	Carson River	2700	70	3.2	22	100	<0.5	13	18	18	<2	<5	49	3.3
16	Carson River	2100	80	<0.5	4	150	<0.5	18	39	14	<2	<5	81	7.3
17	Manufacturing Site	2400	90	<0.5	<2	180	<0.5	48	20	15	<2	<5	120	10
18	Carson River	1900	70	26	17	46	2.0	6	62	200	<2	<5	390	9.3
19	Manufacturing Site	630	60	<0.5	<2	410	<0.5	5.7	30	4	<2	<5	140	36
20	Manufacturing Site	2000	<50	<0.5	<2	150	<0.5	35	52	5	2	<5	68	83
21	Manufacturing Site	7800	320	1.9	4	150	2.8	22	40	23	<2	<4	340	14
22	Oak Ridge	6600	190	1.7	5	120	<0.5	44	36	23	<2	<5	160	88
24	Oak Ridge	6600	250	<0.5	5	89	<0.5	6.3	7	10	<2	<5	31	220
25	Puget Sound	46000	1200	<0.5	2	46	0.7	35	33	31	<2	6	98	35
26	Oak Ridge	88000	340	9.1	10	140	1.9	47	73	82	<2	5	250	100
27	Puget Sound	37000	1100	<0.5	3	33	0.7	39	29	31	<2	5	110	120
29	Manufacturing Site	900	110	<0.5	<2	210	<0.4	16	37	6	<2	<4	88	440
31	Oak Ridge	5000	80	0.59	4	120	<0.5	41	32	16	<2	<5	96	870
32	Manufacturing Site	4700	120	<0.5	2	160	<0.5	190	47	6	<2	<5	78	650
33	Manufacturing Site	<470	120	<0.5	<2	340	<0.5	9.7	31	8	<2	<5	110	1300
45	SRM CRM 033	NR	NR	0.78	130	220	89	100	96	61	89	390	230	6.4
46	SRM CRM 032	NR	NR	81	370	120	130	15	590	4600	170	1300	2600	21
47	SRM NIST 2710	NR	NR	35	630	700	22	39	3000	5500	NR	NR	7000	33
48	SRM CRM 023	NR	NR	NR	380	76	0.92	31	8.9	210	120	NR	94	78
49	SRM CRM 025	NR	NR	130	340	1800	370	440	7.8	1450	520	NR	52	100
50	SRM RTC spec.	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	200
51	SRM RTC spec.	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	400
52	SRM RTC spec.	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	600
53	SRM RTC spec.	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	900
54	SRM RTC spec.	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	1100
62	Spiked Lot 5	3500	210	<0.5	3	28	<0.5	18	11	3	<2	<5	28	23
63	Spiked Lot 23	5700	100	37	11	280	0.9	25	170	140	<2	<5	170	270
64	Spiked Lot 19	630	60	<0.5	<2	410	<0.5	5.7	30	4	<2	<5	140	320
65	Spiked Lot 14	7800	180	0.32	2	41	0.4	16	9	11	<2	<4	74	51
66	Spiked MS-SO-08	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	980
67	Spiked Lot 26	88000	340	9.1	10	145	1.9	47	73	82	<2	5	250	740

CRM = Canadian Reference Material
 RTC = Resource Technology Corporation
 NA = Not Analyzed
 NR = Not Reported by Standard Supplier

Accuracy Summary

In summary, Metorex data did not compare favorably to SRM values, and were not within predicted accuracy determinations. ALSI data compared favorably to SRM values, but were found to be biased low. The comparison between the Metorex field data and the ALSI results suggest that the two data sets are different. Metorex data were found to be both above and below referee laboratory concentrations and therefore there is no implied or suggested bias. The unified hypothesis test provides additional evidence that these two data sets are statistically different, and that Metorex data do not compare to the referee laboratory. Overall, the accuracy evaluations suggest that the Metorex field instrument provides results that are not comparable to the referee laboratory and not within predicted accuracy specifications as determined by SRM reference materials. There may be interferences caused by tested matrices which produce inaccurate results; however, the exact causes of interference remain unknown.

6.1.3 Precision

Precision is usually thought of as repeatability of a specific measurement, and it is often reported as RSD. The RSD is computed from a specified number of replicates. The more replications of a measurement, the higher confidence associated with a reported RSD. Replication of a measurement may be as few as 3 separate measurements to 30 or more measurements of the same sample, depending upon the degree of confidence desired in the specified result. Most samples were analyzed seven times by both Metorex and the laboratory. In some cases, samples may have been analyzed as few as three times and some Metorex results were judged invalid and were not used. This was often the situation when it was believed that the chosen sample, or SRM, was likely to be below the vendor quantitation limit. The precision goal for the referee laboratory, based upon pre-demonstration results, is an RSD of 25% or less. A descriptive evaluation for differences between Metorex RSDs and the referee laboratory RSDs was determined. In Table 6-7, the RSD for each separate sample lot is shown for Metorex compared to the referee laboratory. The average RSD was then computed for all measurements made by Metorex, and this value was compared to the average RSD for the laboratory.

In addition, the precision of an analytical instrument may vary, depending upon the matrix being measured, the concentration of the analyte, and whether the measurement is made for an SRM or a field sample. To

evaluate precision for clearly different matrices, an overall average RSD for the SRMs is calculated and compared to the average RSD for the field samples. This comparison is also included in Table 6-7 for both Metorex and the referee laboratory.

The purpose of this evaluation is to determine the field instrument's capability to precisely measure analyte concentrations under real-life conditions. Instrument repeatability was measured using samples from each of the four different sites. Within each site, there may be two separate matrices, soil and sediment. Not all sites have both soil and sediment matrices, nor are there necessarily high, medium, and low concentrations for each sample site. Therefore, spiked samples were included to cover additional ranges.

Table 6-7 shows results from Oak Ridge, Puget Sound, Carson River, and the manufacturing site. It was thought that because these four different field sites represented different matrices, measures of precision may vary from site to site. The average RSD for each site is shown in Table 6-7 and compared between Metorex and the referee laboratory. SRM RSDs are not included in this comparison because SRMs, while grouped with different sites for purposes of ensuring that the samples remained blind during the demonstration, were not actually samples from that site, and were therefore, compared separately.

The RSDs of various concentrations are compared by noting the RSD of the individual sample lots. The ranges of test samples (field, SRMs, and spikes) were selected to cover the appropriate analytical ranges of Metorex's instrumentation. Average referee laboratory values for sample concentrations are included in Table 6-7, along with SRM values, when appropriate. These are discussed in detail in Section 6.1.2, and are included here for purposes of precision comparison. Sample concentrations were separated into approximate ranges: low, medium, and high, as noted in Table 6-7 and Table 6-1. Because Metorex performed no sample dilution, there are no additional operations that would likely affect precision measurements. Samples reported by Metorex as below their MDL were not included in Table 6-7. There appears to be no correlation between concentration (low, medium, or high) and RSD; therefore, no other formal evaluations of this comparison were performed.

The referee laboratory analyzed replicates of all samples analyzed by Metorex. This was used for purposes of precision comparison to Metorex. RSD for the vendor and the laboratory were calculated individually, and are shown in Table 6-7.

Table 6-7. Evaluation of Precision

Sample Lot No. Metorex and Lab	Avg. Conc. or Reference SRM Value	RSD	Number of Samples	w/in 25% RSD Goal?
OAK RIDGE				
Lot no. 22	81.6 (medium)			
Metorex		21.1%	3	yes
ALSI		9.4%	3	yes
Lot no. 24	207 (medium)			
Metorex		19.9%	7	yes
ALSI		48.4%	7	no
Lot no. 26	77 (medium)			
Metorex		46.6%	7	no
ALSI		13.2%	7	yes
Lot no. 31	947 (high)			
Metorex		0.89%	3	yes
ALSI		13.2%	3	yes
Lot no. 51/ SRM	405 (high)			
Metorex		3.0%	7	yes
ALSI		13.4%	7	yes
Lot no. 65	62.8 (low)			
Metorex		13.0%	7	yes
ALSI		13.5%	7	yes
Lot no. 67	835 (high)			
Metorex		4.3%	7	yes
ALSI		14.8%	7	yes
Oak Ridge Avg. RSD				
Metorex		17.6%		yes
ALSI		20.5%		yes
PUGET SOUND				
Lot no. 11	0.811 (low)			
Metorex		13.8%	3	yes
ALSI		32.7%	7	no
Lot no. 25	16.6 (low)			
Metorex		4.0%	3	yes
ALSI		12.3%	3	yes
Lot no. 27	45.7 (low)			
Metorex		12.8%	7	yes
ALSI		22.2%	7	yes
Lot no. 48/ SRM	77.8 (medium)			
Metorex		5.4%	7	yes
ALSI		32.9%	6	no
Lot no. 50/ SRM	203 (medium)			
Metorex		35.0%	7	no
ALSI		17.7%	7	yes
Lot no. 62	14.6 (low)			
Metorex		7.3%	7	yes
ALSI		28.3%	7	no
Puget Sound/ Avg. RSD				
Metorex		16.4%		yes
ALSI		23.9%		yes
CARSON RIVER				
Lot no. 15	4.23 (low)			
Metorex		3.0%		
ALSI		10.8%	3	yes
		24.5%	7	yes
Lot no. 16	7.13 (low)			
Metorex		12.1%	3	yes
ALSI		13.7%	3	yes

Table 6-7. Continued

Sample Lot No. Metorex and Lab	Avg. Conc. or Reference SRM Value	RSD	Number of Samples	w/in 25% RSD Goal?
Lot no. 18	10.1 (low)			
Metorex		8.2%	3	yes
ALSI		8.0%	7	yes
Lot no. 53/ SRM	910 (high)			
Metorex		2.8%	7	yes
ALSI		35.5%	7	no
Lot no. 54	1120 (high)			
Metorex		2.9%	7	yes
ALSI		21.0%	7	yes
Lot no. 63	169 (medium)			
Metorex		4.8%	7	yes
ALSI		6.6%	7	yes
Carson River/ Avg. RSD				
Metorex		9.0%		yes
ALSI		13.2%		yes
MANUFACTURING SITE				
Lot no. 13	5.91 (low)			
Metorex		5.4%	3	yes
ALSI		15.4%	7	yes
Lot no. 17	10.5 (low)			
Metorex		17.4%	7	yes
ALSI		14.6%	7	yes
Lot no. 19	28.7 (low)			
Metorex		10.2%	3	yes
ALSI		32.2%	7	no
Lot no. 20	63.9 (medium)			
Metorex		10.8%	7	yes
ALSI		25.0%	7	yes
Lot no. 29	374 (high)			
Metorex		6.6%	3	yes
ALSI		17.4%	7	yes
Lot no. 32	592 (high)			
Metorex		5.8%	3	yes
ALSI		12.7%	7	yes
Lot no. 33	1200 (high)			
Metorex		9.1%	7	yes
ALSI		13.3%	7	yes
Lot no. 45/ SRM	6.56 (low)			
Metorex		6.8%	7	yes
ALSI		23.4%	6	yes
Lot no. 47/ SRM	32.6 (low)			
Metorex		6.2%	7	yes
ALSI		27.0%	7	no
Lot no. 49/ SRM	99.8 (medium)			
Metorex		4.1%	7	yes
ALSI		12.5%	7	yes
Lot no. 52/ SRM	608 (high)			
Metorex		3.4%	7	yes
ALSI		21.9%	7	yes
Lot no. 64	285 (medium)			
Metorex		2.6%	7	yes
ALSI		8.8%	7	yes
Lot no. 66	892 (high)			
Metorex		3.7%	7	yes
ALSI		11.2%	7	yes

Table 6-7. Continued				
Sample Lot No. Metorex and Lab	Avg. Conc. or Reference SRM Value	RSD	Number of Samples	w/in 25% RSD Goal?
Manufacturing Site/ Avg. RSD				
Metorex		8.0%		yes
ALSI		16.8%		yes
SUMMARY STATISTICS				
Overall Avg. RSD				
Metorex		9.3%		yes
ALSI		20.6%		yes
Field Samples/ Avg. RSD				
Metorex		10.9%		yes
ALSI		18.7%		yes
SRMs/ Avg. RSD				
Metorex		7.8%		yes
ALSI		22.5%		yes

As noted from Table 6-7, Metorex precision is generally better than the referee laboratory. The single most important measure of precision provided in Table 6-7, overall average RSD, is 20.6% for the referee laboratory, compared to the Metorex average RSD of 9.34%. Both of these RSDs are within the predicted 25% RSD objective for precision expected from both analytical and sampling variance.

In addition, field sample precision compared to SRM precision shows no significant difference between these two sample lots (field sample RSD 18.7% for ALSI and 10.9% for Metorex; SRM RSD 22.5% for ALSI, and 7.8% for Metorex). Differences in these overall RSD numbers suggest differences in the two methods and/or instruments, but not differences attributable to field samples or SRMs. This would suggest that not only was there no difference in analysis of these samples, but that the preparation procedure for the field samples (see Section 4.3.1 for description of field sample homogenization) was very thorough and complete. For purposes of this analysis, spiked samples are considered the same as field samples because these were similar field matrices, and the resulting variance was expected to be equal to field samples. The replicate sample RSDs also confirm the pre-demonstration results, showing that sample homogenization procedures met their originally stated objectives, and that SRM and field sample variation were not significantly different.

There also appears to be no significant site variation between Oak Ridge, Puget Sound, Carson River, and the manufacturing site samples. (See Table 6-7 showing

average RSDs for each of these sample lots. These average RSDs are computed using only the results of the field samples and not the SRMs.) In addition, there appears to be no difference in precision for different concentrations, as noted in the discussion above.

Precision Summary

The precision of the Metorex field instrument is very good, generally better than laboratory precision, and within expected precision variation for soil and sediment matrices. The Metorex field instrument can therefore obtain very precise measurements, equivalent to or even better than laboratory variation covering the entire range of the instrument as determined during this demonstration.

6.1.4 Time Required for Mercury Measurement

The X-MET 2000 was evaluated over a two day period. The amount of time that was needed to setup, prepare and analyze 197 samples, calibrate the analyzer, as well as the time necessary to demobilize, was determined.

Two technicians performed all activities, including sample preparation and analysis activities for 4 batches of mercury-contaminated soil. Setup involved taking the main unit, probe, NiCd batteries and battery charger out of the carrying case, installing a battery in the main unit and connecting the main unit to the electric source. This took approximately 2 minutes. After turning on the instrument, it was allowed to warm up for 15 minutes to ensure repeatable results, and to allow the unit to check its stability

by means of the automatic gain control. The unit was factory calibrated, and no other calibrations were performed during the entire demonstration.

A check sample was run at the start of the demonstration to provide a baseline against which the system could be referenced, and if required, corrected. The check sample was run for 6 minutes. Total setup time including warm-up was about 30 minutes on the first day of the demonstration. The X-MET 2000 analyzer does allow for two types of calibration. Empirical calibration requires a set of standards which have assay values for the elements being analyzed in the unknown sample. Identification calibration requires a set of reference samples to be measured into the memory.

The time required for mercury measurements started with sample setup, and ended when Metorex disconnected the device and placed it back into the carrying case. After setup, sample preparation was performed. Sample preparation involved one technician transferring soil from a 20-mL VOA vial to a 40-mm sample cup covered with polypropylene film. A collar was inserted around the sample cup and a plastic cap was placed on top of the cup to hold soil in place. Dry sandy soil was poured directly into the cup, organic and moist samples were transferred using

a small plastic disposable spoon. It was not necessary to pack the soil into the cup or fill the entire cup for the sample to be analyzed. Sample analysis was done in the top 0.1 mm of the sample. During the demonstration sample preparation took less than 1 minute per sample.

After the instrument was turned on, it went into the measurement menu. In this menu the technician was able to:

- Select the mode of operation
- Change the measurement time
- Make the measurement
- Give a name for the sample to be measured
- Recalculate the analysis or result using another calibration method

Measurements taken with the X-MET 2000 required placing the sample cup on the probe, placing a protective cover over the probe and pressing the start button. A time bar on the display screen appeared indicating the time left for the measurement (Figure 6-3). The time bar box also indicated the type of probe used. The SIPS probe was used for the demonstration (Figure 6-4). The time bar box also indicated the type of probe used.

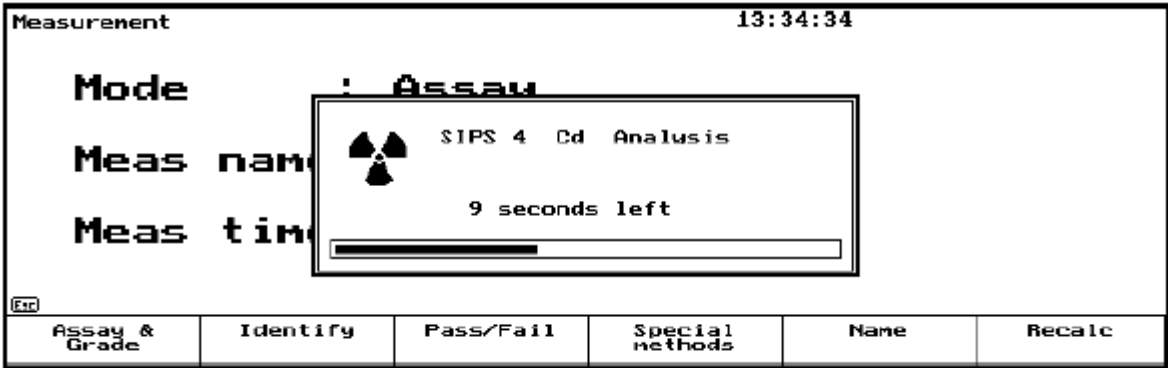


Figure 6-3. X-MET 2000 display screen during measurement.

The X-MET 2000 was able to determine whether one source or two sources were needed. During the demonstration only one source (Cd-109) was needed. However if the measurement was started with one source, but during calculation more information is needed, the X-MET 2000 prompts the technician to measure with the other source. The SIPS probe was used for the demonstration (Figure 6-4).

Measurement times ranging from 30 seconds to 600 seconds can be employed, depending on the data quality needs of the project. As the measurement time increases, the detector collects a larger number of X-rays from the sample. Based on years of experience and sound engineering practice, Metorex determined the measurement times used during the demonstration. The measurement times were 240 seconds per sample for the

Y-12 National Security Complex site (58 samples), Carson River Mercury site (30 samples) and Puget Sound site (34 samples). The measurement time for each of the manufacturing site samples was 180 seconds (75 samples). The technician changed the measurement time by simply pressing the UP/DOWN arrow keys. The measurement time shown on the display screen was the total time required for analysis. After the measurement time had elapsed, the mercury results were displayed on the screen. The X-MET 2000 also allowed the technicians to name the sample, which was shown on the screen along with the results (Figure 6-5). Naming a measurement simply required the technician to press the Name button on the measurement menu. Since no sample name or identification was entered into the main unit during the demonstration, "untitled" appeared on the screen. Sample

results were transcribed from the display screen of the main unit to the chain-of-custody form, and given to the EPA representative prior to leaving the site on day one. On day two, the results were given to the EPA representative shortly after returning to the hotel. Results were available on-site; however, Metorex wanted to ensure there were no transcription errors for some of their data points.

The battery charger allows simultaneous operation of the main unit and charging of both of the batteries. When the main unit is ON, and the charger cable is connected to the main unit, the required operating power is drawn from the charger. The batteries can be simultaneously charged using a normal 16 hour charging. If either battery is switched to the 4 hour quick charge, the other battery is switched off.

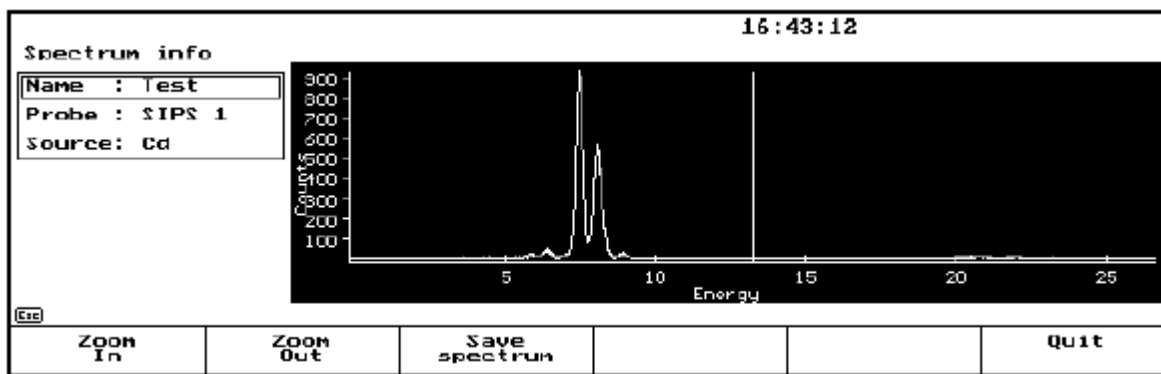


Figure 6-4. X-MET 2000 spectra generated with SIPS probe.

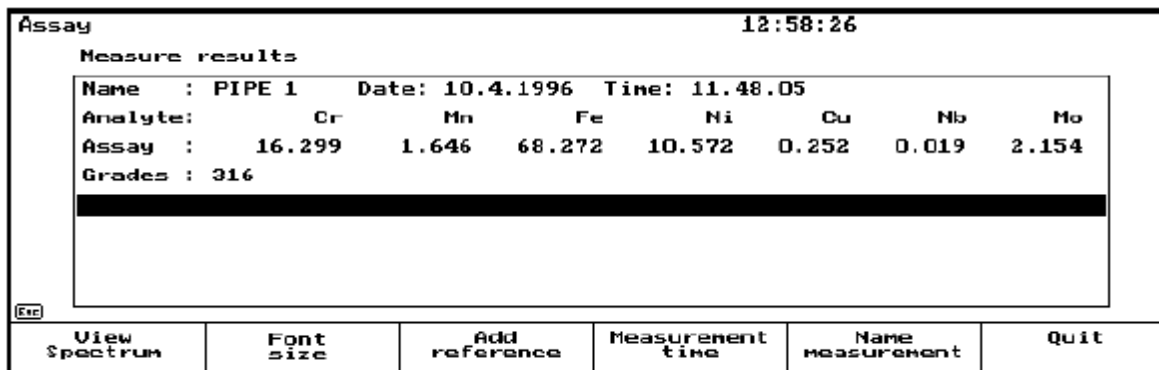


Figure 6-5. X-MET 2000 results screen.

Analysis Time Summary

Metorex required a total 18 hours (36 man hours) for mercury measurements of 197 soil samples during their 2-day demonstration. It should be noted that the second technician was required approximately 25% of the time in order to achieve the sample throughput observed during the demonstration. Table 6-8 indicates the time required to complete mercury measurements using the X-MET 2000 analyzer.

Table 6-8. Mercury Measurement Times

Measurement Activity	Time Required
System Setup	2 minutes
Battery Installation	1 minute
Battery Charge	240 minutes
System Stabilization	15 minutes
Sample Preparation	less than 1 minute per sample
Count Time for Y-12 National Security Samples	4 minutes per sample (58 samples total)
Count Time for Carson River Mercury Site Samples	4 minutes per sample (30 samples total)
Count Time for Puget Sound Samples	4 minutes per sample (34 samples total)
Count Time for Manufacturing Site Samples	3 minutes per sample (75 samples total)
Demobilization	2 minutes

6.1.5 Cost

Background information, assumptions used in the cost analysis, demonstration results, and a cost estimate are provided in Chapter 7.

6.2 Secondary Objectives

This section discusses the performance results for the X-MET 2000 in terms of secondary objectives described in Section 4.1. These secondary objectives were based on observations of the X-MET 2000 and information provided by Metorex.

6.2.1 Ease of Use

Documents the ease of use, as well as the skills and training required to properly operate the device.

Based on observations made during the demonstration, the X-MET 2000 is very easy to operate, requiring one field technician with a high school education, and brief training on the X-MET 2000. The analyzer is a rapid field screening tool. The software is menu driven. No data manipulation is required.

During the demonstration, one technician prepared most of the soil samples while the other technician performed sample analysis. However, both technicians did perform sample preparation and analysis during the two days in the field. One technician could have easily performed both sample preparation and analysis. Two technicians were used during the demonstration in order to increase sample throughput during the limited time on-site. Based on observations and conversations during the field demonstration, the instrument could be easily run by a high school graduate after attending Metorex's brief training course.

Soil samples were provided to Metorex in amber 20-mL VOA vials. In the sample preparation step, soil samples were poured directly from the VOA vial into a polyethylene sample cup with transparent polypropylene film, or was scooped out of the VOA vial with the end of a plastic spoon. It was not necessary to fill the cup to capacity in order to analyze samples. A plastic cap was placed over the polypropylene film to hold the soil and film in-place. The sample cup was placed over the probe window and a safety cover placed over the sample cup. This completed soil sample preparation activities.

After the main unit, keyboard, probe and battery charger were unpacked from the carrying case the technicians prepared the X-MET 2000 for use. A switch at the bottom of the charger was switched to the position of the local line voltage. An extra battery was installed on the top of the charger and left in this position until the ready indicator showed the battery was fully charged. Another battery was installed in the main battery compartment. The probe and keyboard were then connected to the main unit. The ON key was pressed for about 3 seconds until the screen flashed, the instrument started and the power light went

on. After a few seconds, the measurement menu appeared on the display and the instrument was ready for making measurements. Measurements were made by placing the sample cup on the probe and pressing the Start button. After the predetermined 3 or 4 minute measurement time had elapsed, the results were displayed on the screen. For file transfer between the analyzer and PC, a dedicated file transfer program is contained in the instrument. This was not observed during the demonstration. An external printer can also be connected to the X-MET 2000.

When the X-MET 2000 is switched on, the instrument automatically assumes a readiness to start actual measurements. The technicians can perform operations other than measurements by pressing the escape key. This returns the unit to the main menu, from which it is possible to calibrate the instrument, check the settings, generate reports, and perform maintenance on the unit.

6.2.2 Health and Safety Concerns

Documents potential health and safety concerns associated with operating the device.

No significant health and safety concerns were noted during the demonstration. The probe contains radioisotope sources and should never be pointed at any person when the probe is activated.

In addition, the Cd-109 millicurie(20 mCi) source should be replaced every 4 years, but only by authorized personnel.

Health and safety concerns, including chemical hazards, radiation sources, electrical shock, explosion, and mechanical hazards were evaluated.

Potential exposure to radiation from the excitation sources (Cd-109 and Am-241) was the primary health and safety concern during the demonstration. The probe used during the demonstration contained the dual radioactive source configuration of a 20 mCi Cd-109 and a 30 mCi Am-241 source. The Cd-109 source was the only source used during the demonstration. The instrument is sold under a general license, and it is expected that under normal use an operator would not accumulate a radiation dose higher than that from naturally occurring radiation. A health physicist from the Tennessee Department of Environment

and Conservation used a gamma-ray detector to monitor radiation for a half an hour during one day of the demonstration. Background radiation at the site was 5 microrems per hour ($\mu\text{R/hr}$). The Metorex sources are housed in the probe in motor operated turrets. When the Start button is pressed, the source is turned into the measuring position and the measurement is started. After measurements are made, the sources are automatically covered to make the probe radiation safe. During sample analysis, 5 $\mu\text{R/hr}$ was measured 30 centimeters above the protective cover on the probe, and 25 $\mu\text{R/hr}$ was measured on contact with the protective sample cover.

The cadmium source used was originally 20 mCi, and has a half life of about 1.3 years, while the americium source has a half life of 458 years. The cadmium source would have to be replaced every four years and disposed of in accordance with Nuclear Regulatory Commission (NRC) regulations. The replacement of the source and its disposal would have to be done by the manufacturer or their authorized representative.

In addition to the main unit, the SIPS probe and the battery charger conform with low voltage and EMC directives. They meet the requirements of the following standards:

- Safety standards EN 61010-1
- EMC standards EN 50081-1, EN 50082, and EN 61000-3-2

During the demonstration, the operators wore nitrile gloves and safety glasses while transferring the mercury contaminated soil from the VOA vials into the sample cups. SAIC continuously monitored ambient air for mercury using a mercury vapor analyzer. Mercury was not detected (0.000 mg/m^3) in the air or breathing zones during the course of the demonstration.

6.2.3 Portability of the Device

Documents the portability of the device.

The X-MET 2000 is a fully field portable instrument due to its compact size and light weight. It was easy to set up and can be carried anywhere in a water repellent backpack. A sample can be analyzed in less than five minutes.

The X-MET 2000 is a field portable instrument consisting of a main unit, external keyboard, battery and a probe. The system is supported with auxiliary devices including a

spare battery, battery charger, and a water repellent backpack for field transport between sampling locations. Polyethylene sample cups, polypropylene film, and a small sampling tool are required during sample preparation activities. These items can be purchased separately from Metorex or directly from the manufacturer. Five hundred small (approximately 40 mm) sample cups, one roll of polypropylene film and a small sample tool can fit easily into a small box. The principal components are housed in a padded carrying case that is 610 mm by 610 mm by 152 mm. The main unit weighs 5.8 kilograms (kg) and is 360 mm by 290 mm by 100 mm. The SIPS probe weighs 1.6 kg and is 225 mm by 250 mm by 76 mm. The SIPS probe also is equipped with a 290-mm cable. During the demonstration, a fully charged NiCd battery lasted for 4 hours and 10 minutes. The instrument was also run off a 115 volt electric line.

According to Metorex, the main unit and the SIPS probe will operate between 0 and 50 °C. In addition the main unit, probe and charger can operate at 20 °C with 95% relative humidity and no condensation. During the demonstration relative humidity was recorded as high as 98.3%. The main unit and probe are sealed according to IP55 requirements; however, they should not be exposed to rain.

The main unit and probes are designed to endure the following stresses:

- Vibration 2g, 10Hz to 150 Hz
- Bump 25g

where “g” is the acceleration of gravity.

The instrument is designed to resist shocks during transport and operation. Dropping the instrument may damage the sensitive components especially the probe. During measurement, even smaller vibrations may lead to inaccurate results if the probe is influenced.

During the demonstration, Metorex performed sample preparation and analysis under a tent. The instrument was set up in 2 minutes on a six-foot-long folding table. The small battery operated system could be repackaged for movement to a remote sample location in minutes, or could be easily carried to another sample location in a backpack and operated for about 4 hours on 1 NiCd battery.

No solvents or acids were used for sample preparation. The only additional waste generated was the sample cups and polypropylene film used during analysis of intrusive samples. Finally, even though the instrument contains radioisotopes, it can be shipped by express courier as reportable quantity excepted package Class 7.

6.2.4 Instrument Durability

Evaluates the durability of the device based on its materials of construction and engineering design.

The X-MET 2000 was well designed and constructed for durability. Metorex has been a manufacturer of alloy analysis instrumentation since the 1960's.

There are over 5000 analyzers in use throughout the world. The X-MET 2000 contains sources housed in a metal turret with additional shielding inside the probe to ensure the containment of radiation. Based on Metorex literature, the main unit and probe were constructed of aluminum and stainless steel. Based on observations during the demonstration, the main unit and probe were well constructed and durable. During the two days in which the instrument was observed there was no downtime, maintenance, or repairs. The equipment was not apparently affected by the two days of almost continuous rain and relative humidity as high as 98.3%. The instrument was, however, operated under a tent.

6.2.5 Availability of Vendor Instruments and Supplies

Documents the availability of the device and spare parts.

The X-MET 2000 is readily available for rental, lease, or purchase. Another analyzer if needed, can be received within 30 days of order placement. There are over 60 distributors in 50 countries.

Sample cups and polypropylene film are the only supplies needed to analyze samples intrusively and are available from several supply firms.

The Metorex X-MET 2000 analyzer evaluated during the demonstration was shipped from Finland and held up in customs in Nashville, TN for 3 days. Another instrument could have been shipped from within the U.S. if the

equipment was not released from customs in time. The delay was due to a declaration issue related to the foam packaging material inside the carrying case. Even though the instrument was not on-site until the second day of the demonstration, there was no delay in the schedule.

During the demonstration, the main unit, probe, keyboard and disposable supplies did not have to be replaced. If a replacement main unit or probe was required, Metorex claimed it could have been shipped from within the U.S. by express courier and held for pick-up the next day. The instrument must be held for pick-up at the local express courier office, and cannot be delivered to any location. This is required because the instrument contains radioisotopes. The local express courier office was located

20 minutes away from the site. In general, no time would be lost picking up another unit at a local express courier office, rather than having it delivered the next day to the site by 10:30 a.m. Many express courier offices are open as early as 8 a.m.

In general, the X-MET 2000 analyzer is available within 30 days of order placement.

The disposable supplies (sample cups and polypropylene film) if needed for intrusive analysis could be obtained from the manufacturer and shipped overnight directly to the site by express courier. Metorex claims the analyzer does not require any soil standards.

Chapter 7

Economic Analysis

The purpose of the economic analysis was to estimate the total cost of mercury measurements at a hypothetical site. The cost per analysis was estimated; however, because the cost per analysis would decrease as the number of samples analyzed increased, the total capital cost was also estimated and reported. Because unit analytical costs are dependent upon the total number of analyses, no attempt was made to compare the cost of field analyses with the X-MET 2000 to the costs associated with the referee laboratory. "Typical" unit cost results, gathered from analytical laboratories, were reported to provide a context in which to review the X-MET costs. No attempt was made to make a direct comparison between these costs for different methods because of differences in sample throughput, overhead factors, total equipment utilization factors, and other issues that make a head-to-head comparison impractical.

This chapter describes the issues and assumptions involved in the economic analysis, presents the costs associated with field use of the X-MET 2000, and presents a cost summary for a "typical" laboratory performing sample analyses using the reference method.

7.1 Issues and Assumptions

Several factors can affect mercury measurement costs. Wherever possible in this chapter, these factors are identified in such a way that decision-makers can independently complete a project-specific economic analysis. Metorex offers three options for potential X-MET users: 1) purchase of the analyzer, 2) monthly rental (10% of the sales price per month for a short term rental), and 3) analyzer leasing depending on current interest rates. (Metorex, 2003a) Because site and user requirements vary significantly, all three of these options are discussed

to provide each user with the information to make a case-by-case decision.

A more detailed cost analysis was performed on the equipment rental because this case represents the most-frequently encountered field scenario. The results of that cost analysis are provided in Section 7.2.

7.1.1 Capital Equipment Cost

The X-MET 2000 analyzer housed with Cd-109 and Am-241 consists of the following key components; main unit, SIPS probe, 2-NiCd batteries, battery charger, Serial RS-232 cable, field carrying case, software package, accessories, and a user's manual. An external keyboard and a serial to parallel converter cable are optional parts. (Metorex 2003a)

The cost quoted by Metorex does not include freight costs to ship the instrument to the user location, or the license (radioactive source) that may be needed to operate the instrument. The license that was needed to operate the analyzer in the state of Tennessee cost \$900. The first and last month's rental cost is required for rental and lease agreements. (Metorex, 2003a) Operator training is included in the purchase price, however a training session is available for \$1000 per day for anyone renting the analyzer. (Metorex, 2003a)

7.1.2 Cost of Supplies

The cost of supplies is minimal, based on the supplies required to analyze demonstration samples. Requirements vary depending upon whether in-situ or intrusive analysis is being performed. For purposes of this cost estimate, only supplies required to analyze soil samples intrusively are factored into the cost estimate. Disposable supplies are not required for in-situ analysis. The supplies used

during the demonstration consisted of three consumable items which were:

- XRF sample cups (one per sample)
- Polypropylene film
- Plastic spoons

The purchase prices and supply sources were obtained from Metorex. Because the user cannot return unused or remaining portions of supplies, no salvage value was included in the cost of supplies. (Metorex, 2003a) PPE supplies were assumed to be part of the overall site investigation or remediation costs; therefore, no PPE costs were included as supplies.

7.1.3 Support Equipment Cost

During the demonstration, the X-MET 2000 analyzer was operated using both AC power and a NiCd battery. The instrument operated for 4 hours and 10 minutes using one NiCd battery. Only the battery charger requires AC (110/220 volt at 1 amp).

Because of the large number of samples expected to be analyzed during the demonstration, EPA provided support equipment, including tables and chairs, for the field technician's comfort. In addition, EPA provided a tent to ensure that there were no delays in the project due to inclement weather. These costs may not be incurred in all cases. However, such equipment is frequently needed in field situations, so these costs were included in the overall cost analysis.

7.1.4 Labor Cost

The labor cost was estimated based on the time required for X-MET 2000 setup, sample preparation, sample analysis, summary data preparation, and instrument packaging at the end of the day. Setup time covered the time required to take the analyzer out of its packaging, set up all components, and ready the device for operation. Sample preparation involved transferring samples into the XRF sample cups. Sample preparation was completed easily, requiring less than one minute per sample. Sample analysis was the time required to analyze all samples and submit a data summary. The data summary was strictly a tabulation of results in whatever form the vendor chose to provide. In this case, the vendor transcribed results from the main unit's computer screen to the field COC forms. (A printer was not available in the field.) The time required to perform all tasks was rounded to the nearest minute. However, for the economic analysis, times were rounded to the nearest hour, and it was assumed that a field technician who had worked for a fraction of a day would be

paid for an entire 8-hour day. Based on this assumption, a daily rate for a field technician was used in the analysis.

During the demonstration, EPA representatives evaluated the skill level required for the two field technicians to analyze and report results for mercury samples. Based on these field observations, a high school graduate with brief training specific to the X-MET 2000 would be qualified to operate the analyzer. For the economic analysis, an hourly rate of \$15 was used for a field technician. A multiplication factor of 2.5 was applied to labor costs to account for overhead costs. Based on this hourly rate and multiplication factor, and an 8-hour day, a daily rate of \$300 was used for the economic analysis. Monthly labor rates are based on the assumption of an average of 21 work days per month. This assumes 365 days per year, and non work days totaling 113 days per year (104 weekend days and 9 holidays; vacation days are discounted assuming vacations will be scheduled around short-term work or staff will be rotated during long projects). Therefore, 252 total annual work days are assumed.

7.1.5 Investigation-Derived Waste Disposal Cost

Metorex was instructed to segregate its waste into three categories during the demonstration: 1) general trash; 2) lightly contaminated PPE and wipes; and 3) contaminated soil (both analyzed and unanalyzed). The general trash was not included as IDW and is not discussed in this document.

Lightly contaminated wastes consisted primarily of used nitrile gloves and Kim-wipes. The gloves were discarded for one of two reasons: 1) they posed a potential health and safety risk (holes or tears), or 2) the technician needed to perform other tasks (e.g., using cell phone). The rate of waste generation was in excess of what would be expected in a typical application of this instrument. The normal technician should not need to frequently use a cell phone to correspond with clients. In addition, the EPA evaluators occasionally contributed used gloves to this waste accumulation point. Wipes were used primarily to clean any spilled soil off of the table and to clean off any moist or organic material adhering to the plastic spoons which were used to transfer soil into the sample cups. In cases where cross contamination is not a major concern (e.g., field screening or in-situ analysis), lesser amounts of waste would likely be generated.

Contaminated soil consisted primarily of soil placed in the XRF sample cups covered with polypropylene film. The sample is not destroyed during preparation and analysis;

therefore it is possible to send the samples off-site for confirmatory analysis.

7.1.6 Costs Not Included

Items for which costs were not included in the economic analysis are discussed in the following subsections, along with the rationale for exclusion of each. Any licensing fees required for the radionuclide source were not included, as they vary from state to state.

Oversight of Sample Analysis Activities. A typical user of the X-MET would not be required to pay for customer oversight of sample analysis. EPA representatives observed and documented all activities associated with sample analysis during the demonstration. Costs for this oversight were not included in the economic analysis because they were project specific. For the same reason, costs for EPA oversight of the referee laboratory were also not included in the analysis.

Travel and Per Diem for Field Technician. Field technicians may be available locally. Because the availability of field technicians is primarily a function of the location of the project site, travel and per diem costs for field technicians were not included in the economic analysis.

Sample Collection and Management. Costs for sample collection and management activities, including sample homogenization and labeling, are site specific and, therefore, not included in the economic analysis. Furthermore, these activities were not dependent upon the selected reference method or field analytical tool. Likewise, sample shipping, COC activities, preservation of samples, and distribution of samples were specific requirements of this project that applied to all vendor technologies and may vary from site to site. None of these costs was included in the economic analysis.

Items Costing Less than \$10. The costs of inexpensive items, such as paper towels, were not included in the economic analysis.

Documentation Supplies. The costs of digital cameras used to document field activities were not included in project costs. These were considered project-specific costs that would not be needed in all cases. In addition, these items can be used for multiple projects. Similarly, the cost of supplies (logbooks, copies, etc.) used to document field activities was not included in the analysis because they are project specific.

Health and Safety Equipment. Costs for rental of the mercury vapor analyzer and the purchase of PPE were considered site specific and, therefore, not included as costs in the economic analysis. Safety glasses and disposable gloves were required for sample handlers and would likely be required in most cases. However, these costs are not specific to any one vendor or technology. As a result, these costs were not included in the economic analysis.

Mobilization and Demobilization. Costs for mobilization and demobilization were considered site specific, and not factored into the economic analysis. Mobilization and demobilization costs actually impact laboratory analysis more than field analysis. When a field economic analysis is performed, it may be possible to perform a single mobilization and demobilization. During cleanup or remediation activities, several mobilizations, demobilizations, and associated downtime costs may be necessary when an off-site laboratory is used because of the wait for analytical results.

7.2 X-MET 2000 Costs

This section presents information on the individual costs of capital equipment, supplies, support equipment, labor, and IDW disposal for the X-MET 2000.

7.2.1 Capital Equipment Cost

During the demonstration, the X-MET 2000 was operated for 2 days and was used to analyze 197 samples. Table 7-1 summarizes the X-MET 2000 capital costs for the three procurement options: rental, lease, and purchase. Figure 7-1 shows the relative costs for the basic capital equipment. These costs reflect the X-MET 2000 housed with Cd-109 and Am-241 sources. As would be expected, Table 7-1 clearly shows that leasing is the most cost-effective option (in terms of capital costs), followed by rental, for short-term projects. As project duration (or use on multiple projects) approaches two years, the purchase option is the most cost-effective. These scenarios cover only capital cost, not the cost of optional or user-supplied equipment, supplies, support equipment, labor, and IDW disposal.

The X-MET 2000 (with Cd-109 and Am-241 sources) sells for \$34,240, including the main unit, probe, two NiCd batteries, serial RS cable, field carrying case, software package and a keyboard. The cadmium source (20 mCi) used during the demonstration needs to be replaced about every 4 years. The cost of replacing the source is \$4500.

Table 7-1. Capital Cost Summary for the X-MET 2000

Item	Quantity	Unit Cost (\$)	Total Cost for Selected Project Duration				
			1-Month	3-Month	6-Month	12-Month	24-Month
Purchase X-MET	1	\$34,240	\$34,240	\$34,240	\$34,240	\$34,240	\$34,240
Monthly Rental of X-MET ^a	1	\$3,400	\$3,400	\$10,200	\$20,400	\$40,800	\$81,600
Monthly Lease of X-MET ^b	1	\$1,570	\$1,570	\$4,710	\$9,420	\$18,880	\$37,680
Purchase Printer (Optional)	1	\$150	\$150	\$150	\$150	\$150	\$150

^a Ten percent of purchase price.

^b \$1,570 per month (24-month lease with \$1 buyout).

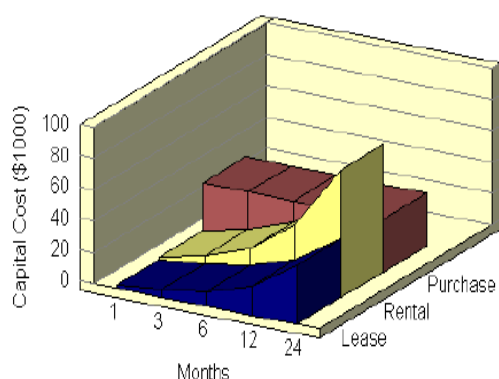


Figure 7-1. Capital equipment costs.

7.2.2 Cost of Supplies

Supplies used during the demonstration included XRF sample cups and polypropylene film. NIST soil SRMs were not used during the demonstration and according to Metorex are not required to operate the analyzer.

7.2.3 Support Equipment Cost

Metorex was provided with a 10x10 foot tent for protection from inclement weather during the demonstration. It was also provided with one table and two chairs for use during sample preparation and analytical activities. The rental cost for the tent (including detachable sides, ropes, poles, and pegs) was \$270 per week. The rental cost for the table and two chairs for one week totaled \$6. Total support equipment costs were \$276 per week for rental.

For longer projects, purchase of support equipment should be considered. Two folding chairs would cost approximately \$40. A 10x10 foot tent would cost between \$260 and \$1,000, depending on the construction materials and the need for sidewalls and other accessories (e.g.,

sand stakes, counter weights, storage bag, etc.). A cost of \$800 was used for this cost analysis. A folding table would cost between \$80 and \$250, depending on the supplier. For purposes of this cost analysis, \$160 was used. Total purchase costs for support equipment are estimated at \$1,000.

7.2.4 Labor Cost

Two technicians were utilized for 2 days during the demonstration to complete sample preparation and analyses. Based on a labor rate of \$600 per day, total labor cost for application of the X-MET 2000 was \$1200 for the 2-day period. However, the observer estimates that the second technician was required only 25% of the time in order to achieve the sample throughput observed during the demonstration. Labor costs assume qualified technicians are available locally, and that no hotel or per diem costs are applicable. Table 7-2 summarizes labor costs for various operational periods, assuming 21 work days per month (on average), 252 work days per year, and one technician per job site. The costs presented do not include supervision and quality assurance, because these would be associated with use of any analytical instrument, and are a portion of the overhead multiplier built into the labor rate.

Table 7-2. Labor Costs

Item	Months				
	1	3	6	12	24
Technician	\$6,300	\$18,900	\$37,800	\$75,600	\$151,200
Supervisor/QC	NA	NA	NA	NA	NA
Total	\$6,300	\$18,900	\$37,800	\$75,600	\$151,200

7.2.5 Investigation-Derived Waste Disposal Cost

Metorex generated PPE waste and soil waste including sample cups and polypropylene film. The PPE waste was charged to the overall project due to project constraints. The minimum waste volume is a 5-gallon container. Mobilization and container drop-off fees were \$1,040; a 5-gallon soil waste drum cost was \$400. (These costs were based on a listed waste stream with hazardous waste number U151). The total IDW disposal cost was \$1,440. These costs may vary significantly from site to site, depending on whether the waste is classified as hazardous or nonhazardous and whether sample material is generated that requires disposal. Table 7-3 presents IDW costs for various operational periods, assuming that waste generation rates were similar to those encountered during the demonstration.

Table 7-3. IDW Costs

Item	Months				
	1	3	6	12	24
Drop Fee	\$1,040	\$3,120	\$6,240	\$12,480	\$24,960
Disposal	\$400	\$1,200	\$2,400	\$4,800	\$9,600
Total	\$1,440	\$4,320	\$8,640	\$17,280	\$34,560

7.2.6 Summary of X-MET 2000 Costs

The total cost for performing mercury analysis is summarized in Table 7-4. This table reflects costs for projects ranging from 1-24 months. The rental option was used for estimating the equipment cost.

Table 7-4. Summary of Rental Costs for the X-MET 2000

Item	Quantity	Unit	Unit Cost (\$)	Total Cost for Selected Project Duration				
				1- Month	3- Month	6- Month	12- Month	24- Month
Capital Equipment								
Monthly Rental of X-MET 2000	1	NA	\$3,400	\$3,400	\$10,200	\$18,000	\$36,000	\$72,000
Support Equipment								
Table (optional) - weekly	1	each	\$5	\$20	\$60	\$120	\$160	\$160
Chairs (optional) - weekly	2	each	\$1	\$10	\$25	\$40	\$40	\$40
Tent (for inclement weather only) - weekly	1	each	\$270	\$800	\$800	\$800	\$800	\$800
Total Support Equipment Cost	--	-----	-----	\$830	\$885	\$960	\$1,000	\$1,000
Labor								
Field Technician (person day	1	hour	\$38	\$6,300	\$18,900	\$37,800	\$75,600	\$151,200
IDW								
Container and Drop Fee			\$1,040	\$1,040	\$3,120	\$6,240	\$12,480	\$24,960
Disposal	NA	week	\$400	\$400	\$1,200	\$2,400	\$4,800	\$9,600
Total IDW Costs	—	-----	-----	\$1,440	\$4,320	\$8,640	\$17,280	\$34,560
Total Cost				\$11,970	\$34,305	\$65,400	\$129,880	\$258,760

Additionally, capital costs for equipment rental exceed those for purchase at approximately 10 months, so rental is not as cost-effective as purchase for projects exceeding this duration. Finally, a lease agreement may be a cost-effective alternative, compared to either rental or

purchase for projects lasting less than 21 months. At that point, equipment purchase may be more cost effective; however, the decision on which purchase option to utilize should be made on a case-by-case basis.

Table 7-5 summarizes costs for the actual demonstration. Note that the 1-month rental cost of the X-MET 2000 was used for capital costs.

Table 7-5. X-MET 2000 Costs by Category

Category	Category Cost (\$)	Percentage of Total costs
Instrument	\$3,400	51.9%
Supplies	\$240	3.7%
Support Equipment	\$276	4.2%
Labor	\$1,200	18.3%
IDW Disposal	\$1,440	22.0%
Total	\$6,556	100.0%

Note, the percentages in Table 7-5 are rounded to one decimal place; the total percentage is 100.1%.

The cost per analysis based upon 197 samples when renting the X-MET 2000 is \$33.28 per sample. The cost per analysis for the 197 samples, excluding instrument cost is \$16.02 per sample.

7.3 Typical Reference Method Costs

This section presents costs associated with the reference method used to analyze the demonstration samples for mercury. Costs for other project analyses are not covered. The referee laboratory utilized SW-846 Method 7471B for all soil and sediment samples. The referee laboratory performed 421 analyses over a 21-day time period.

A typical mercury analysis cost, along with percent moisture for dry-weight calculation, is approximately \$35. This cost covers sample management and preparation, analysis, quality assurance, and preparation of a data package. The total cost for 197 samples at \$35 would be \$6,895. This is based on a standard turnaround time of 21-calendar days. The sample turnaround time from the laboratory can be reduced to 14, 7, or even fewer calendar days, with a cost multiplier between 125% to 300%, depending upon project needs and laboratory availability. This results in a cost range from \$6,895 to \$20,685. The laboratory cost does not include sample packaging, shipping, or downtime caused to the project while awaiting sample results.

Chapter 8

Summary of Demonstration Results

As discussed previously in this ITVR, the Metorex X-MET 2000 was evaluated by having the vendor analyze 197 soil and sediment samples. These 197 samples consisted of high-, medium-, and low-concentration field samples from four sites, SRMs, and spiked field samples. Table 8-1 provides a breakdown of the numbers of these samples for each sample type, and concentration range or source. Collectively, these samples provided the different matrices, concentrations, and types of mercury needed to perform a comprehensive evaluation of the X-MET 2000.

8.1 Primary Objectives

The primary objectives of the demonstration were centered on evaluation of the field instrument and performance in relation to sensitivity, accuracy, precision, time for analysis, and cost. Each of these objectives was discussed in detail in previous chapters, and is summarized in the following paragraphs. The overall demonstration results suggest that the experimental design was successful for evaluation of the Metorex X-MET 2000. Quantitative results were reviewed. It was determined that this instrument was not comparable to standard analyses performed by the laboratory. Specifically, while Metorex results were determined to be very precise, they were not found to be as accurate as laboratory-analyzed data.

The two primary sensitivity evaluations performed for this demonstration were the MDL and PQL. Following procedures established in 40 CFR Part 136, MDL is between 16.5 and 26.9 mg/kg. This is only a calculated determination, but it is also supported by results of analyses performed at the lower level of detection, which suggest that this is close to noise level of the instrument when analyzing soils and sediments. The equivalent MDL for the referee laboratory is 0.0026 mg/kg. The calculated MDL is

only intended as a static estimation and not a true test of instrument sensitivity.

The PQL for the Metorex field instrument was more difficult to define. The low standard calculations suggest that a PQL for the Metorex field instrument may be somewhere around 64 mg/kg. Metorex results, however, are highly variable, even at higher concentrations. As previously noted, this is because of the instrument's inaccuracy, as demonstrated by having only 19% of the SRM results within the 95% prediction interval and having percent differences between the reported and true value often greater than 100%. Therefore, given the definition associated with a PQL with a defined accuracy and precision, an actual PQL for the Metorex field instrument is difficult to estimate. The referee laboratory PQL, determined as part of the laboratory analysis, is 0.005 mg/kg with a %D of <10%, based upon a lower calibration standard.

Accuracy was evaluated by comparison to SRMs and comparison to the referee laboratory analysis for field samples. This included spiked field samples for evaluation of additional concentrations not otherwise available. Metorex data did not compare well to SRM values and were not within predicted accuracy determinations. The results from the X-MET 2000 were compared to the 95% prediction interval for the SRM materials. The percentage of Metorex analyses within the 95% prediction interval was only 19%, with $n = 63$. The comparison between the Metorex field data and the referee laboratory results also suggest that the two data sets are, in fact, different. Metorex data were outside the range of statistical equivalency. Metorex data were found to be both above and below referee laboratory concentrations and therefore, there is no implied or suggested bias. In determining the number of results significantly above or below the value

reported by the referee laboratory, 22 of 32 average results were greater than 50% different. Overall, the accuracy evaluations suggest that the Metorex field instrument provides results that are not comparable to the referee laboratory, and not within predicted accuracy specifications as determined by SRM reference materials. There are likely interferences caused by tested matrices which produce inaccurate results, however, these interferences remain unknown. The reason for this postulate is because it did not appear to be random variation that caused these fluctuations, as noted in the precision discussion below.

Precision was determined by analysis of replicate samples. The precision of the Metorex field analyzer is generally better than the referee laboratory. The single most important measure of precision, overall average RSD for all 32 sample lots, is 20.6% for the referee laboratory, compared to the Metorex average RSD of 9.34%. Both of these RSDs are within the predicted 25% RSD objective for precision; expected from both analytical and sampling variance. Precision was not affected by sample concentration or matrix.

Time measurements were based on the length of time the operator spent performing all phases of the analysis, including setup, calibration, and sample analyses (including all reanalyses). Metorex analyzed 197 samples in 1,350 minutes (18 hours times 60 minutes times 1.25 analysts)

over two days, which averaged to 6.9 minutes per sample result. Based on this, an operator could be expected to analyze 69 samples (8 hours x 60 minutes ÷ 6.9 minutes/sample) in an 8-hour day.

Cost of the Metorex sample analyses included capital, supplies, labor, support equipment, and waste disposal. The cost per sample was calculated both with and without the capital cost of the instrument included. This was performed because the first sample requires the instrument purchase, and as the sample number increases, the cost per sample would decrease. A comparison of the field Metorex cost to off-site laboratory cost was not made. To compare the field and laboratory costs correctly, it would be necessary to include the expense to the project while waiting for analyses to return from the laboratory (potentially several mobilizations and demobilizations, stand-by fees, and other aspects associated with field activities).

Table 8-2 summarizes the results of the primary objectives.

8.2 Secondary Objectives

Table 8-3 summarizes the results of the secondary objectives.

Table 8-1. Distribution of Samples Prepared for Metorex and the Referee Laboratory

Site	Concentration Range	Sample Type			SRM
		Soil	Sediment	Spiked Soil	
Carson River (Subtotal = 30)	Low (1-500 ppb)	0	0	0	0
	Mid (0.5-50 ppm)	9	0	0	0
	High (50->1,000 ppm)	0	0	7	14
Puget Sound (Subtotal = 34)	Low (1 ppb - 10 ppm)	3	0	0	0
	High (10-500 ppm)	0	10	7	14
Oak Ridge (Subtotal = 58)	Low (0.1-10 ppm)	0	7	0	0
	High (10-800 ppm)	13	10	14	14
	General (5-1,000 ppm)	33	0	14	28
Manufacturing (Subtotal = 75)					
Subtotal		58	27	42	70

Table 8-2. Summary of X-MET 2000 Results for the Primary Objectives

Demonstration Objective	Evaluation Basis	Performance Results X-MET 2000	Reference Method
Instrument Sensitivity	MDL. Method from 40 CFR Part 136.	Between 16.5 and 26.9 mg/kg	0.0026 mg/kg
	PQL. Low concentration SRMs or samples.	Estimated at 64 mg/kg	0.005 mg/kg
Accuracy	Comparison to SRMs, field, and spiked samples covering the entire range of the instrument calibration.	The Metorex field instrument did not attain accuracy specifications comparable to the referee laboratory. Overall, accuracy was determined to be outside expectations for most analytical instrumentation. This included comparisons to both SRMs and field samples.	
Precision	Determined by analysis of replicate samples at several concentrations.	Overall RSD was computed to be 9.34%, compared to the referee laboratory RSD of 20.6%. This is a combined measure of precision which includes sampling and aliquoting variations. Metorex's precision is better than the referee laboratory analysis, and is not affected by matrix or concentration.	
Time per Analysis	Timed daily operations for 2 days and divided the total time by the total number of analyses.	Two technicians performed all setup, calibration checks, sample preparation and analysis, and equipment demobilization. (It should be noted that the second technician was required approximately 25% of the time in order to achieve the sample throughput observed during the demonstration.) Individual analyses took 3 or 4 minutes each, but the total time per analysis averaged approximately 6.9 minutes per sample.	
Cost	Costs were provided by Metorex and independent suppliers of support equipment and supplies. Labor costs were estimated based on a salary survey. IDW costs were estimated from the actual costs encountered at the Oak Ridge demonstration.	The cost per analyses based upon 197 samples, when renting the X-MET 2000, is \$33.28 per sample. The cost per analysis for the 197 samples, excluding capital cost, is \$16.02 per sample. The total cost for equipment rental and necessary supplies during the demonstration is estimated at \$6,556. The cost breakout by category is: capital rental costs, 51.9%; supplies, 3.7%; support equipment, 4.2%; labor, 18.3%; and IDW, 22.0%.	

Table 8-3. Summary of X-MET 2000 Results for the Secondary Objectives

Demonstration Objectives	Evaluation Basis	Performance Results
Ease of Use	Field observations during the demonstration.	Based on observations made during the demonstration, the X-MET 2000 is very easy to operate, requiring one field technician with a high school education, and brief training on the X-MET 2000. The analyzer is a rapid field screening tool. The software is menu driven. No data manipulation is required.
Health and Safety Concerns	Observation of equipment, operating procedures, and equipment certifications during the demonstration.	No significant health and safety concerns were noted during the demonstration. The probe contains radioisotope sources and should never be pointed at any person when the probe is activated. In addition, the Cd-109 (20 mCi) source should be replaced every 4 years only by authorized personnel.
Portability of the Device	Review of device specifications, measurement of key components, and observation of equipment setup and tear down before, during, and after the demonstration.	The X-MET 2000 is a fully field portable instrument due to its compact size and light weight. It was easy to set up, and can be carried anywhere in a water repellent backpack. A sample can be analyzed in less than five minutes.
Instrument Durability	Observation of equipment design and construction, and evaluation of any necessary repairs or instrument downtime during the demonstration.	The X-MET 2000 was well designed and constructed for durability. Metorex has been a manufacturer of alloy analysis instrumentation since the 1960's.
Availability of Vendor Instruments and Supplies	Review of vendor website and telephone calls to the vendor after the demonstration.	The X-MET 2000 is readily available for rental, lease, or purchase. A replacement analyzer if needed, can be received within 30 days of order placement. There are over 60 distributors on 50 continents. Sample cups and polypropylene film are the only supplies needed to analyze samples intrusively, and are available from several supply firms.

Section 9

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Appendix A

Metorex Comments

Overall Conclusions

1. The XRF technique provides a quick, easy and low cost method to determine the concentration of environmental contamination in soil samples. In fact, it can be used to analyze the concentration of multiple analytes.
2. The precision of the data obtained was excellent. This indicates that shorter measurement times can be used to allow even faster throughput.
3. The accuracy of the data in the range from the MDL to the high end of the calibration was quite good with 9 of 15 samples in this range showing no significant difference from the reference laboratory result (see discussion below). At the extremes of the calibration, the nature of the calibration samples provided is critical.

Precision

The precision of XRF measurements is determined mainly by the number of counts in the peak of the spectrum. This is in turn determined by the measurement time used. In this demonstration measurement times of 240 seconds and 180 seconds were used for the various samples. The standard deviation of the SRM's was 9.34% while the standard deviation of the field samples was 10.9%. This indicates that there were very little difference in the

treatment and handling of the samples during this demonstration.

Accuracy

The accuracy of the assay is determined largely by the standards used to prepare the empirical calibration. Errors in the determination of the concentration of the analyte in the calibration samples will be transferred to the assay of the unknowns. Thus, it is important to have good assays of the samples used for the calibration. Also, it is important to have standards which cover the entire range of the unknowns. The lack of standards at the high concentration in fact contributes to the inaccuracy of the assay at the high end of the range. The highest calibration sample for the Oak Ridge calibration was 420 mg/kg; for the Carson River calibration was 850 mg/kg and for the manufacturing sight was 774 mg/kg. Therefore, any samples with concentrations higher than these values can be expected to have inaccurate assays. In addition, there were no calibration samples available for the Puget Sound samples, those samples were analyzed using the Carson River calibration which may not have a similar matrix. At the low end of the assay results below the MDL (about 20 mg/kg) are suspect. If one looks at the data between the MDL and the values of the high calibration sample the accuracy was quite good with 9 of 15 samples (or 60%) not having significant differences from the value obtained by the reference laboratory (in addition in the case of lot 64, the standard deviation of both Metorex and reference

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laboratory were very small making the difference limits quite tight and while the difference between the values was only 15.1% the test failed - if one includes this lot, the accuracy improves to 10 out of 15 lots or 66.6%).

The chart in Figure A-1 illustrates the correlation of the values reported on the X-Met 2000 vs. the values reported

by the reference laboratory. The correlation across the range is quite good. However, the fact that the slope of this plot is not one indicates that there is an inaccuracy in the slope of the calibration curve, possibly caused by inaccuracy in the assay of one or more of the calibrations samples.

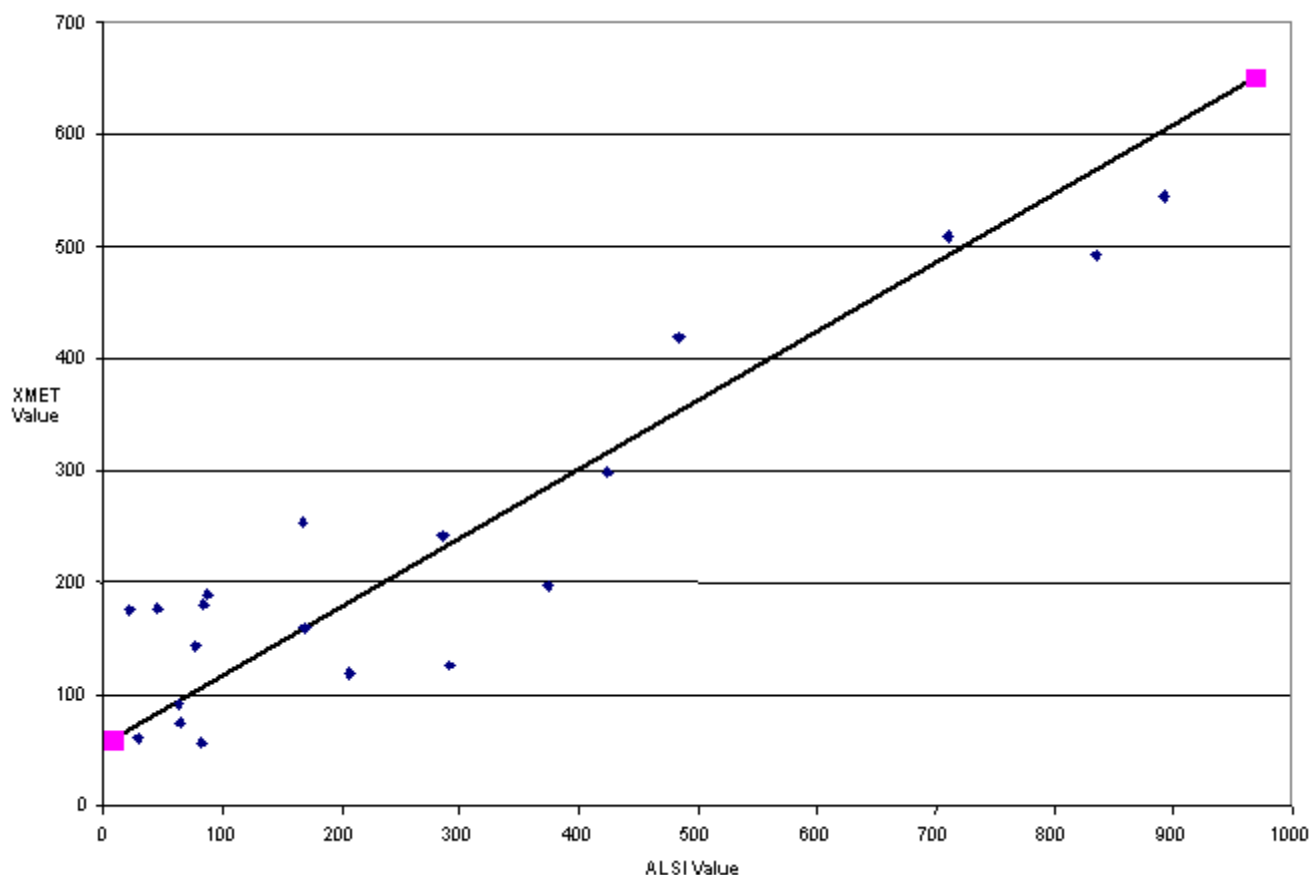


Figure A-1. Correlation of Metorex versus laboratory results.

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Appendix B Statistical Analysis

Two separate hypothesis tests were used to compare the referee laboratory samples to the vendor tested samples. This appendix details the equations and information for both of these statistical analyses. For purposes of this appendix, we have chosen to call the test comparing sample populations using a separate calculation for each sample lot the “hypothesis test,” and the statistical comparison of the entire sample set (all 32 separate sample lots) analyzed by the vendor and the laboratory the “unified hypothesis test,” also known as an “aggregate analysis” for all of the sample lots.

Hypothesis Test

A hypothesis test is used to determine if two sample populations are significantly different. The analysis is performed based on standard statistical calculations for hypothesis testing. This incorporates a comparison between the two sample populations assuming a specified level of significance. For establishing the hypothesis test, it was assumed that both sample sets are equal. Therefore, if the null hypothesis is rejected, then the sample sets are not considered equal. This test was performed on all sample lots analyzed by both Metorex and the referee laboratory. H_0 and H_a , null and alternative hypothesis respectively, were tested with a 0.01 level of significance (LOS). The concern related to this test is that, if two sample populations have highly variable data (poor precision), then the null hypothesis may be accepted because of the test’s inability to exclude poor precision as a mitigating factor. Highly variable data results in wider acceptance windows, and therefore, allows for acceptance of the null hypothesis. Conclusions regarding this analysis are presented in the main body of the report.

To determine if the two sample sets are significantly different, the absolute value of the difference between the

laboratory average \bar{x}_L and the vendor average \bar{x}_V is compared to a calculated μ . When the absolute value of the difference is greater than μ , then the alternate hypothesis is accepted, and the two sets (laboratory and vendor) are concluded to be different.

To calculate μ , the variances for the laboratory data set and the vendor data set are calculated by dividing their standard deviations by the number of samples in their data set. The effective number of degrees of freedom is then calculated.

$$f = \frac{(V_L + V_V)^2}{\left(\frac{V_L^2}{n_L + 1}\right) + \left(\frac{V_V^2}{n_V + 1}\right)} - 2$$

Where:

f	= effective number of degrees of freedom
V_L	= variance for the laboratory results
n_L	= number of samples for the laboratory data set
V_V	= variance for the vendor results
n_V	= number of samples for the vendor data set.

The degrees of freedom (f) is used to determine the appropriate “t” value and used to calculate μ at the 0.01 level of significance using the following:

$$\mu = t_{1-(0.005/f)} \sqrt{V_L + V_V}$$

Unified Hypothesis Test

For a specified vendor, let Y_{ij} be the measured Hg concentration for the j^{th} replicate of the i^{th} sample for $i=1,2,\dots,I$ and $j=1,2,\dots,J_i$. Let $X_{ij} = \log(Y_{ij})$, where log is the logarithm to the base 10. Define $\bar{x}_{i\log}$ to be the average over all log replicates for the i^{th} sample given by:

$$\bar{X}_{i\log} = J_i^{-1} \log \sum_{j=1}^{J_i} X_{ij}$$

Denote the estimate of the variance of the log replicates for the i^{th} sample to be:

$$s^2 = \left(\sum_{i=1}^I (J_i - 1) \right)^{-1} \log \sum_{i=1}^I \sum_{j=1}^{J_i} (X_{ij} - \bar{X}_{i\log})^2$$

Now for the reference laboratory, let Y'_{ij} be the measured Hg concentration for the j^{th} replicate of the i^{th} sample for $i=1,2,\dots,I'$ and $j=1,2,\dots,J'_i$. Denote the reference laboratory quantities X'_{ij} , \bar{x}'_i , and s'^2 defined in a manner similar to the corresponding quantities for the vendor.

Assumptions: Assume that the vendor measurements, Y_{ij} , are independent and identically distributed according to a lognormal distribution with parameters μ_i and σ^2 . That is, $X_{ij} = \log(Y_{ij})$ is distributed according to a normal distribution with expected value μ_i and variance σ^2 . Further, assume that the reference laboratory measurements, Y'_{ij} , are independent and identically distributed according to a lognormal distribution with parameters μ'_i and σ'^2 .

The null hypothesis to be tested is:

$$H_0: \mu_i = \mu'_i + \delta, \text{ for some } \delta \text{ and } i = 1, \dots, I$$

against the alternative hypothesis that the equality does not hold for at least one value of i .

The null hypothesis H_0 is rejected for large values of:

$$\chi^2_{I-1} = \frac{\sum_{i=1}^I (\bar{X}_{i\log} - \bar{X}'_{i\log} - \delta)^2 \div (J_i^{-1} + J'^{-1}_i)}{s^2_{pool}}$$

Where χ^2_{I-1} is approximately a chi-square random variable with $(I-1)$ degrees of freedom:

$$\delta = I^{-1} \log \sum_{i=1}^I (\bar{X}_{i\log} - \bar{X}'_{i\log})$$

and

$$s^2_{pool} = \frac{s^2 \log \sum_{i=1}^I (J_i - 1) + s'^2 \log \sum_{i=1}^{I'} (J'_i - 1)}{\sum_{i=1}^I (J_i - 1) + \sum_{i=1}^{I'} (J'_i - 1)}$$

Critical values for the hypothesis test are the upper percentile of the chi-square distribution with $(I-1)$ degrees of freedom obtained from a chi-square table.

Results of Unified Hypothesis Test for Metorex

SAIC performed a unified hypothesis test analysis to assess the comparability of analytical results provided by Metorex and those provided by ALSI. Metorex and ALSI both supplied multiple assays on replicates derived from a total of 32 different sample lots, be they field materials or reference materials. The Metorex and ALSI data from these assays formed the basis of this assessment.

The statistical analysis is based on log-transformed (logarithm base 10) data and uses a chi-square test for equality of Metorex and ALSI population means for given sample lot. Equality of variances is assumed.

Initially, the null hypothesis tested was that, on average, Metorex and ALSI would produce the same results within a given sample lot. This hypothesis is stated as

$$H_{10}: (\text{Metorex lot log mean}) = (\text{ALSI lot log mean})$$

H_{10} was strongly rejected in that the chi-square statistic was 3,163.97, which exceeds the upper 99th percentile of the chi-square distribution with 32 degrees of freedom having a value of 53.49.

The null hypothesis was rejected in part because Metorex results tended to exceed those from ALSI for the same sample lot. To explore this effect, the null hypothesis was revised to included a bias term in the form of

$$H_{20}: (\text{Metorex lot log mean}) = (\text{ALSI lot log mean}) + (\text{delta}),$$

where delta is a single value that does not change from one sample lot to another, unlike the lot log means. H_{20} was rejected strongly in that the chi-square statistic was 2,659.90, which exceeded the upper 99th percentile of the chi-square distribution with 31 degrees of freedom with a value of 52.19. In this analysis, delta was estimated to be 0.265 in logarithmic (base 10) space, which indicates an average upward bias for Metorex of $10^{0.265}=1.840$ or about 84%.

For both hypotheses, the large values of the chi-square test statistics summarize the disagreement between the Metorex and ALSI analytical results. Furthermore, a review of the statistical analysis details indicates that the overall

discordance between Metorex and ALSI analytical results cannot be traced to the disagreement in results for one or two sample lots.

Summary information on these analyses is provided in Table B-1. The p-value can be considered as a significance level. This is a calculated value and usually when one sets a p-value (e.g., 95% confidence level which translates to a p-value of 0.05), this value is used to test the level of significance for comparison. As noted in the Table B-1 the p-value is calculated from the test statistics and therefore it can be seen that because the p-value is so small (< 0.000000) the two sample populations are considered to be non-equivalent and hence the large chi-square value.

Table B-1. Unified Hypothesis Test Summary Information

Hypothesis	Total Sample Lots	Excluded Lot	DF	s^2_{pool}	Delta	Chi-square	P-value
H_{10}	32	None	32	0.00940	0.0000	3,163.97	0.000000
H_{20}	32	None	31	0.00940	0.2651	2,659.90	0.000000